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Southwest Research Inst., San Antonio, TX

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Jun 84

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June 1984

EPA METHOD STUDY 16,
METHOD 606--PHTHALATE ESTERS

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by

John D. Millar
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Contract 68-03-2606

Robert L. Graves and Edward L. Berg, Project Officers

Quality Assurance Branch
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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This report describes the results obtained and data analysis from an interlaboratory method study of EPA Method 606 (Phthalate Esters). The method is designed to analyze for six phthalate esters: dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, benzylbutyl phthalate, bis-2-ethylhexyl phthalate, and di-n-oxtyl phthalate.

The study design required the analyst to dose six waters with each of six mixtures of the six phthalates. The six dosing levels represented three Youden pairs, one each at a low, an intermediate, and a high level. A total of 16 laboratories participated in the study.

The method was studied to estimate the accuracy and precision that can be expected, including effects on accuracy and precision of analysis of different matrices. In addition, results of method detection limit and analytical curve studies and qualitative assessments of the method based upon comments by the participating laboratories are included.

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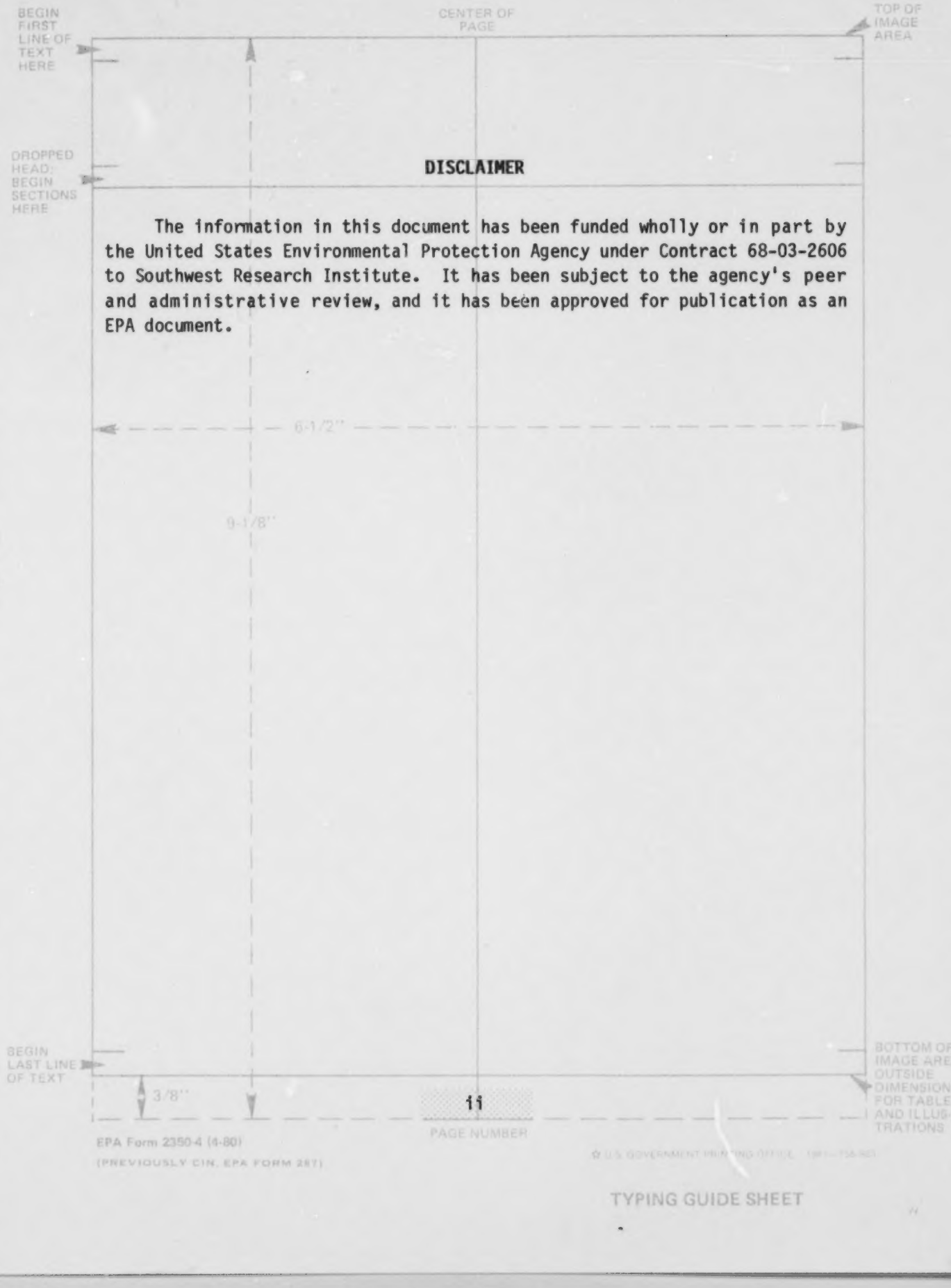

DISCLAIMER

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati, conducts research to:

- develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste;
- investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microorganisms in water;
- conduct studies to determine the responses of aquatic organisms to water quality;
- conduct an agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication of EMSL-Cincinnati reports the results of EPA's method study for the following priority pollutants:

Dimethyl phthalate
Diethyl phthalate
Di-n-butyl phthalate
Benzylbutyl phthalate
bis-2-Ethylhexyl phthalate
Di-n-octyl phthalate

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of assistance in monitoring and controlling pollution in the environment.

R. L. Booth
Director, EMSL-Cincinnati

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ABSTRACT

This report describes the results obtained and data analysis from an interlaboratory method study of EPA Method 606 (Phthalate Esters). The method is designed to analyze for six phthalate esters: dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, benzylbutyl phthalate, bis-2-ethylhexyl phthalate, and di-n-octyl phthalate, in water and wastewater. As tested here, the method utilizes three 60-mL extractions with dichloromethane, cleanup/separation on a Florisil or alumina column, and injection into a gas chromatograph equipped with an electron capture detector.

The study design required the analyst to dose six waters with each of six mixtures of the six phthalates. The six dosing levels represented three Youden pairs, one each at a low, an intermediate, and a high level. The six waters used were a laboratory pure water, a finished drinking water, and a surface water, all collected by the participant, and three low-background industrial effluents provided by the prime contractor. A total of 16 laboratories participated in the study.

The method was studied to estimate the accuracy and precision that can be expected, including effects on accuracy and precision of analysis of different matrices. In addition, results of method detection limit and analytical curve studies and qualitative assessments of the method based upon comments by the participating laboratories are included.

The work was performed between September 1978 and December 1981 under Contract 68-03-2606

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SECTION 1

INTRODUCTION

EPA first promulgated guidelines [1] establishing test procedures for the analysis of pollutants in 1973, following the passage of the Federal Water Pollution Control Act in 1972 by Congress. Pursuant to the amendment and publication of these guidelines, EPA entered into a Settlement Agreement--the Consent Decree--which required the study and, if necessary, regulation of 65 "priority" pollutants and classes of pollutants of known or suspected toxicity to the biota. Subsequently, Congress passed the Clean Water Act of 1977 [2], mandating the control of toxic pollutants discharged into ambient waters by industry.

In order to facilitate the implementation of the Clean Water Act, EPA selected 129 specific toxic pollutants, 113 organic and 16 inorganic, for initial study. The organic pollutants were divided into 12 categories based on their chemical structure. Analytical methods were developed by EPA for these 12 categories through in-house and contracted research. These analytical methods may eventually be required for the monitoring of the 113 toxic pollutants in industrial wastewater effluents, as specified by the Clean Water Act of 1977.

As a logical subsequence to that work, an interlaboratory study was conducted to obtain accuracy and precision statements for Method 606 (Phthalate Esters) [3] based upon multilaboratory data. This report describes the work performed, presents the data acquired, and gives the conclusions drawn from the collaborative effort.

The six compounds undergoing analysis in the interlaboratory study were dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), benzylbutyl phthalate (BBP), bis-2-ethylhexyl phthalate (2EHP), and di-n-octyl phthalate (DOP).

The laboratories participating in this study were the 16 lowest bidders from the list of qualifying laboratories that responded to the request for bids. Qualifications were established based upon information submitted by the laboratories and by experience with the laboratories in

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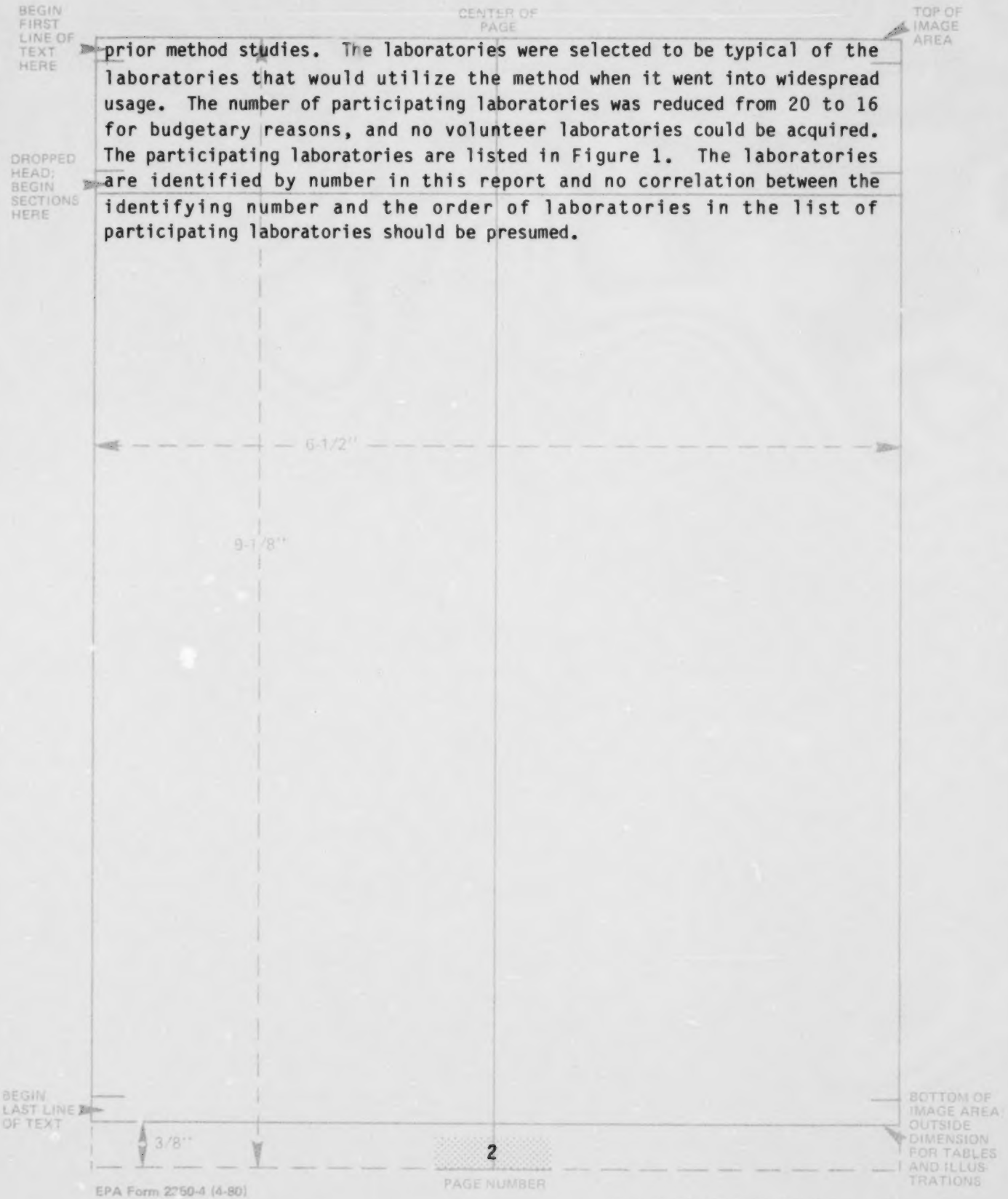
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prior method studies. The laboratories were selected to be typical of the laboratories that would utilize the method when it went into widespread usage. The number of participating laboratories was reduced from 20 to 16 for budgetary reasons, and no volunteer laboratories could be acquired. The participating laboratories are listed in Figure 1. The laboratories are identified by number in this report and no correlation between the identifying number and the order of laboratories in the list of participating laboratories should be presumed.
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Tonawanda, New York 14150

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Syracuse Research Corporation
Merrill Lane
Syracuse, New York 13210

Systems, Science, and Software
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San Diego, California 92121

Technical Services, Inc.
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Jacksonville, Florida 32201

Wilson Laboratories
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Salina, Kansas 67401

Figure 1. Participating laboratories

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SECTION 2

SUMMARY

As a result of the collaborative study conducted and the data analysis, the following conclusions can be drawn concerning EPA Method 606 (Phthalate Esters).

- The accuracy of the method could generally be expressed as a linear function of the true concentration. The regression equations are shown in Table 1.
- The precision of the method could generally be expressed as a linear function of the mean recovery, both as single-analyst and overall standard deviations. These regression equations are also shown in Table 1.
- The percent recovery of the method differed from that obtained during the developmental phase, especially for DMP and DEP. Recoveries at the midrange of the concentrations studied ranged from 33 to 93%, with a median of 78.5. Twenty-nine of the thirty-six recoveries were at or above 70%.
- There was considerable variability among the results, especially for DMP, DEP, and 2EHP. High relative standard deviations were determined for both 2EHP and DOP in laboratory pure water.
- Six water types were used in this study: laboratory pure, finished drinking, surface, and three relatively interference-free industrial effluents. Differences in variability were noted for DEP and 2EHP and differences in mean recovery for DOP as a result of the comparison across water types. These differences were noted in comparison with the values obtained for laboratory pure water.
- The principal problem for the collaborators was in attaining a consistent background and avoiding interferences, especially in the elution regions of DMP, DEP, and 2EHP. Other problem areas noted included Kuderna-Danish concentration, which some analysts believed to be the principal source of analyte losses.

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TABLE 1. ACCURACY AND PRECISION EQUATIONS

Water type Range, ug/L	Dimethyl phthalate 1.75-26.9	Diethyl phthalate 1.70-27.4	Di-n-butyl phthalate 2.48-34.9	Benzyl butyl phthalate 0.70-12.2	bis-2-Ethylhexyl phthalate 5.07-55.6	Di-n-octyl phthalate 8.49-52.1
Laboratory Pure						
Accuracy	X = 0.73c+0.17	X = 0.70c+0.13	X = 0.79c+0.17	X = 0.82c+0.13	X = 0.53c+2.02	X = 0.35c-0.71
Precision						
Overall	S = 0.44X+0.31	S = 0.45X+0.11	S = 0.29X+0.06	S = 0.25X+0.07	S = 0.73X-0.17	S = 0.62X+0.34
Single analyst	SR = 0.26X+0.14	SR = 0.27X+0.05	SR = 0.23X+0.20	SR = 0.26X+0.04	SR = 0.80X-2.54	SR = 0.38X+0.71
Finished Drinking						
Accuracy	X = 0.85c-0.08	X = 0.72c+0.29	X = 0.75c+0.35	X = 0.92c+0.07	X = 0.74c+1.72	X = 0.76c+0.65
Precision						
Overall	S = 0.44X+0.18	S = 0.40X+0.06	S = 0.28X+0.20	S = 0.37X-0.01	S = 0.48X+0.97	S = 0.43X+1.45
Single analyst	SR = 0.30X+0.30	SR = 0.28X+0.05	SR = 0.20X+0.36	SR = 0.32X-0.03	SR = 0.36X+0.46	SR = 0.20X+5.44
Surface						
Accuracy	X = 0.72c+0.44	X = 0.77c+0.23	X = 0.78c+0.40	X = 0.93c+0.21	X = 0.50c+7.12	X = 0.69c-0.48
Precision						
Overall	S = 0.38X+0.24	S = 0.42X+0.46	S = 0.31X+0.31	S = 0.30X+0.07	S = 0.24X+5.94	S = 0.40X-0.11
Single analyst	SR = 0.35X-0.03	SR = 0.26X+0.15	SR = 0.31X-0.06	SR = 0.32X-0.10	SR = -0.01X+9.71	SR = 0.26X-0.64
Ind. Effluent 1						
Accuracy	X = 0.66c+0.30	X = 0.86c+0.36	X = 0.74c+0.35	X = 0.79c+0.07	X = 0.68c+3.32	X = 0.64c-0.31
Precision						
Overall	S = 0.41X+0.03	S = 0.56X+0.35	S = 0.32X+0.24	S = 0.34X+0.08	S = 0.41X+4.42	S = 0.44X-0.53
Single analyst	SR = 0.28X+0.07	SR = 0.39X-0.09	SR = 0.35X-0.31	SR = 0.25X+0.12	SR = 0.15X+6.94	SR = 0.29X-0.48
Ind. Effluent 2						
Accuracy	X = 0.73c-0.23	X = 0.77c-0.12	X = 0.84c+0.07	X = 0.85c+0.12	X = 0.81c+2.73	X = 0.66c-1.41
Precision						
Overall	S = 0.31X+0.29	S = 0.48X+0.28	S = 0.32X+0.55	S = 0.23X+0.17	S = 0.64X-0.65	S = 0.36X+0.90
Single Analyst	SR = 0.27X+0.14	SR = 0.31X+0.07	SR = 0.18X+1.10	SR = 0.26X-0.06	SR = 0.24X+6.04	SR = 0.25X+0.47
Ind. Effluent 3						
Accuracy	X = 0.69c+0.22	X = 0.87c-0.25	X = 0.78c+0.10	X = 0.83c+0.10	X = 0.47c+11.52	X = 0.60c-1.66
Precision						
Overall	S = 0.44X+0.45	S = 0.66X+0.03	S = 0.34X+0.27	S = 0.28X+0.06	S = -0.12X+17.61	S = 0.37X+1.02
Single analyst	SR = 0.26X+0.59	SR = 0.49X-0.30	SR = 0.28X-0.13	SR = 0.27X	SR = -0.23X+17.79	SR = 0.21X+2.69

c = actual concentration

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SECTION 3

DESCRIPTION OF STUDY

The study design was based on Youden's original plan [4] for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs where each sample of a pair has a slightly different concentration of the constituent. The analyst is directed to do a single analysis and report one value for each sample, as if for a normal, routine sample.

In this study, samples were prepared as concentrates in sealed glass ampules and shipped to the analyst with portions of final effluents from manufacturing plants from three relevant industries. Each participating laboratory was responsible for supplying laboratory pure water, a finished drinking water, and a surface water, thus giving a total of six water matrices involved in the study. The analyst was required to add an aliquot of each concentrate to a volume of water from each of the six waters and submit the spiked water to analysis. Three pairs of samples were used. One pair contained the substances at what was considered to be equivalent to a low level for the industrial effluents; a second pair contained the substances at an intermediate level; and the third pair contained the substances at a high level.

TEST DESIGN

A summary of the test design using Youden's nonreplicate technique for X and Y samples is given below:

1) Three Youden pairs were used for each parameter with the deviation from the mean of each pair being at least 5% but not more than 20%.

2) The three Youden pairs were spread over a usable and realistic range with the lowest level estimated to be near the detection limit in the industrial effluent with the highest background of electron capture-sensitive materials.

3) Analyses were performed in six waters. Therefore, each laboratory was to generate 36 data points for each compound.

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Three of the waters were selected from relevant industries as determined from the information contained in a memorandum of December 29, 1978 from M. Dean Neptune, Analytical Programs, Effluent Guidelines Division to R. B. Schaffer, director, Effluent Guidelines Division, through W. A. Telliard, chief, Energy and Mining Branch.

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4) Thirty-six concentrates in sealed glass ampules were shipped with approximately 12 liters (3 gallons) of each of the three industrial effluents to the 16 laboratories. The concentrations of substances in the ampules were unknown to the participants.

5) Each participant was supplied with a copy of Method 606 and supplementary instructions relative to spiking procedure, cleanup column to be used, GC column and detector to be used, and GC injection technique.

6) To commence an analysis, the analyst was instructed to open an ampule, add 1 mL of concentrate to 1 L of water, then analyze as per instructions.

7) Each sample was to be analyzed once.

8) Before the formal study began, each participant was sent a pair of ampules (not one of the pairs used in the study) for a trial analysis by Method 606. After submitting data from these analyses to SwRI, all participants met in Cincinnati to discuss problems encountered during the trial run.

9) Fifty ampules of each concentrate prepared were supplied to the project officer.

PREPARATION OF SAMPLES, WASTEWATER SELECTION AND PROCUREMENT

The phthalate esters used to prepare sample concentrates were obtained from Chem Service, Inc. The detailed protocol for concentrate and ampule production was reviewed and approved by the project officer before ampule production commenced. Salient points of the protocol are described in the following paragraph.

Sample concentrates were prepared by dissolving precisely weighed (analytical balance) amounts in acetone in Class A volumetric flasks. Where dilutions were required, Class A volumetric glass pipettes were used to transfer the required volumes. All glassware had been fired overnight at approximately 400°C before use. The volumes transferred were never less than 4 mL. Solutions were put into brown, borosilicate glass ampules,

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chilled, and heat-sealed. The sealed ampules were stored in paperboard boxes at room temperature until shipped to participants.

Before each concentrate was used to fill ampules, the concentrations of substances were compared with a standard that had been prepared from separate weighings of the substances. Three ampules taken at random from the ampules produced were checked against the same external standard mentioned immediately above. These verification checks served to prevent gross errors from being committed; the true values were assumed to be those established by the weighings of substances for concentrate preparation. It was rare to find a verification analysis which deviated more than 5% from the true value. The true values for all test substances are given in Table 2.

TABLE 2. TRUE CONCENTRATIONS IN STUDY SAMPLES
(1 mL concentrate in 1 L water; µg/L)

Compound	Lowest pair		Medium pair		Highest pair	
Ampule lot number	3	1	4	6	2	8
dimethyl phthalate	1.746	2.241	9.603	12.326	20.952	26.892
diethyl phthalate	2.107	1.695	12.642	10.170	27.391	22.035
di-n-butyl phthalate	3.493	2.475	13.971	9.901	34.928	24.752
benzylbutyl phthalate	0.696	0.872	4.178	5.232	9.749	12.208
bis-2-ethylhexyl phthalate	5.071	6.946	20.285	27.786	40.570	55.571
di-n-octyl phthalate	17.671	14.083	70.685	56.333	106.027	84.499

Sources of the industrial effluents selected for the interlaboratory study were as follows:

Industrial effluent 1--textile plant
Industrial effluent 2--organics and plastic plant
Industrial effluent 3--petroleum refining and petrochemical complex.

Effluents from 11 plants were examined before the above three were selected. The rejected effluents showed background that made the determination of the lowest Youden pair impossible and the determination of one or both of the other pairs doubtful. In the effluents selected, background peaks representing fractional ppb quantities of DMP, BBP, and 2EHP were found in effluent 1. Effluent 3 gave background peaks representing fractional ppb BBP and DOP and 12 ppb 2EHP. All three effluents had peaks eluting so near to the eluting times of the phthalates that their presence could cause some difficulties in quantitating at the lowest spike levels. This was especially true for effluent 3 with respect to DMP, DEP, and DBP.

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The wastewaters were collected in two 55-gallon untreated iron drums, shipped to SwRI, pooled, and reshipped to participants in 1-gallon glass containers obtained from Burdick and Jackson, Inc.

ANALYSIS AND REPORTING

In addition to admonitions to follow Method 606 procedure (Appendix B), supplementary instructions were sent to participants at the time the trial run ampules were shipped. Participants were advised how to dose the water (1 mL per L) and to make injections of extract into the GC using the solvent-flush technique described by Burke [5]. Only electron capture detectors were to be used. Also, the stipulation was made that all pertinent GC recorder charts be sent with the data submitted for the trial run and the formal tests to follow.

At the Cincinnati conference, trial run data were presented and a step-by-step discussion of the method was given. The most common errors (calculation, standards preparation, and improper expression of results) were pointed out. At the meeting, the following supplementary instructions were given:

1) If interference from elemental sulfur is encountered in analyzing the extracts, use mercury to remove the interference, following the procedure given in Method 608 (Organochlorine Pesticides and PCBs).

2) Use extreme care in preparing calibration curves, especially for DMP and DEP, because of the nonlinear responses observed for these substances with electron capture detection.

After the Cincinnati conference, a follow-up letter was sent to each participant requesting that the example data calculation sheets and data summary sheets that were enclosed be used during the study. The same letter requested that the final report include information on the following:

1) method of quantitating;

2) sources of standards;

3) source of surface water and the nature of any possible contaminants;

4) suggestions as to how Method 606 could be improved.

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DISTRIBUTION OF SAMPLES

A single shipment of 36 ampules was made by overnight air express to all laboratories. No instance of ampule breakage during shipment was reported. However, some participants reported shortages or received empty, unbroken ampules and others accidentally broke ampules during the study. Replacement ampules were provided in these cases.

The water matrices were also shipped by overnight air express, each participant receiving approximately 12 liters (3 gallons) of each of the three industrial effluents. The time required to collect and distribute the effluents was about three weeks. No breakage in transit occurred. Several gallons were broken or otherwise made unusable through laboratory mishaps. Replacement shipments were made in these instances.

STABILITY OF SAMPLES

Specifications within the scope of work required that concentrates for spiking had to exhibit satisfactory stability for 45 days before the trial run ampules could be sent out and for 90 days before shipments for the formal study could commence. These milestones were passed without significant difficulty. The stability measurements consisted of comparing the highest level of the middle Youden pair against freshly prepared standards. Four ampules were withdrawn at random at 0-, 45-, and 90-day periods. Triplicate GC injections of the properly diluted contents were made and the average value obtained compared to the freshly prepared standards. Deviations from the true value varied in a manner similar to that observed during the verification analyses. Thus, stability was considered to be satisfactory.

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SECTION 4

TREATMENT OF DATA

The objective of this interlaboratory study was to obtain information about the accuracy and precision associated with measurements generated by Method 606. This objective was met through the use of statistical analysis techniques designed to extract and summarize the relevant information about accuracy and precision from the data reported by the participating laboratories. The statistical techniques employed in the data reduction process are similar to the techniques suggested in the ASTM Standard Practice D2777-77.

The algorithms required to perform the statistical analyses have been integrated into a system of computer programs referred to as IMVS (Interlaboratory Method Validation Study). The analyses performed by IMVS [6] include several tests for the rejection of outliers (laboratories and individual data points), summary statistics by concentration level for mean recovery (accuracy), overall and single-analyst standard deviation (precision), determination of the linear relationship between mean recovery and concentration level, determination of the linear relationship between the precision statistics and mean recovery, and a test for the effect of water type on accuracy and precision.

A detailed description of each of the statistical analysis procedures is presented below.

PREPROCESSING

An initial review of the data was performed to determine if a systematic error was evident in the data that could be identified and legitimately corrected prior to data analysis. Chromatograms and supporting data were investigated to verify that the analyses were run under the proper conditions and that calculations were accurate and supportable. Where an anomaly existed, such as a series of results that were different from the true values by one or more orders of magnitude, the analyst was contacted, told that there was an apparent error, and asked to check his values. No indication was given as to the nature of the inconsistency in order not to prejudice the results. If an error was

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found, the corrected values were used in the data analysis. If the analyst reported no error could be found, the data were allowed to stand as reported. The results from one laboratory, 605, were deleted from the study after review. This laboratory was unable to satisfactorily account for their laboratory interferences and their results were considered unusable.

All analyses reported as less than a detection limit were removed from the data set prior to insertion into the computer program along with results that the analysts noted as influenced by spillage or loss of sample. The data set thus prepared was utilized in the package of programs supplied by the sponsor for analysis of collaborative study data.

REJECTION OF OUTLIERS

Spurious data points are always a part of any set of data collected during an interlaboratory test program. It is important to identify and remove these data points because they can lead to values of summary statistics which are not representative of the general behavior of the method. However, some erratic behavior in the data may be directly related to some facet of the method under the study. Therefore, spurious data points should not be removed indiscriminantly, and any points that are removed should be clearly identified since further investigation of the analytical conditions related to the outliers might be of value. Data rejected as outliers for this study as a result of any of the following tests for outliers have been identified by the symbol "*" in the raw data tables in Appendix A.

YOUDEN'S LABORATORY RANKING PROCEDURE

In some cases the analytical values reported by a specific laboratory are so consistently high or low that a large systematic error may be attributed to that laboratory. These data are not representative of the method and should be rejected. Youden's [4] ranking test for outlying laboratories was applied separately to data from each of the waters used in this study. Since six water types were used in this study, the laboratory ranking procedure was applied to these six different subsets of the data. Each laboratory ranking test was performed at the 5% level of significance.

The Youden laboratory ranking procedure requires a complete set of data from every laboratory within a given water type. Missing data from laboratory i for water type j were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory i for water type j and concentration level C_k, it is assumed that

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$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk}$$

where β_j and γ_j are fixed parameters which determine the effect of water type j, L_i is the systematic error due to laboratory i and ε_{ijk} is the random within laboratory error. Taking natural logarithms, it follows that

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \varepsilon_{ijk}$$

which is a linear regression model with dependent variable $\ln X_{ijk}$ and independent variable $\ln C_k$. (Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types.")

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampules in each water type. The predicted values $\ln X_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $\hat{X}_{ijk} = \exp(\widehat{\ln X_{ijk}})$. (For complete details of this procedure see Reference 7.)

If the ranking test rejected a laboratory for a specific water type, then all of the laboratory data for that water type were rejected as outliers. The rejected values were excluded from all the remaining analyses. In addition, after completion of the laboratory ranking procedure, the predicted values created to fill in for the missing data were rejected and excluded from further analyses.

TESTS FOR INDIVIDUAL OUTLIERS

The data remaining after the laboratory ranking procedure were grouped by water type. For each water type, the data were broken down into six subsets defined by the six concentration levels (ampules) used in the study. For each subset of the data, all missing, zero, "less than" and "nondetect" data were rejected. Next, the test for individual outliers constructed by Thompson [8] and suggested in the ASTM Standard Practice D2777-77 was applied to the data using a 5% significance level. If an individual data point was rejected based on this test, it was removed from the subset, and the test was repeated using the remaining data in the subset. This process was continued until no additional data could be rejected.

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STATISTICAL SUMMARIES

Several summary statistics were calculated using the data remaining for each concentration level after the outlier rejection tests were performed. These summary statistics include: the number of retained data points, the mean recovery, accuracy as a percent relative error, the absolute overall standard deviation, the percent relative overall standard deviation, the absolute single-analyst standard deviation, and the percent relative single-analyst standard deviation. The basic formulas used to calculate these statistics are presented below where X_1, X_2, ..., X_n denote the values of the n retained data points for a specific concentration level.

Mean Recovery (X):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

The usual notation of $\bar{X}$ is not used for the mean in this report to accommodate the computer-generated tables.

Accuracy as a % Relative Error:

$$\%RE = \frac{\bar{X} - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2}$$

and

Percent Relative Overall Standard Deviation:

$$\%RSD = \left(\frac{S}{\bar{X}}\right) \times 100$$

The overall standard deviation S indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in an interlaboratory study. However, a measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This

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single-analyst precision, denoted by SR, was estimated for each Youden pair by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2}$$

where m - the number of complete sets of Youden pair observations remaining after outliers have been removed,
D_i - the difference between the observations in the i^{th} Youden pair,
$\bar{D}$ - average of the D_i values.

The percent relative single-analyst standard deviation was calculated by

$$\%RSD\text{-}SR = \frac{SR}{X^*} \times 100$$

where X* is the average of the two mean recovery statistics corresponding to the two concentration levels defining the particular Youden pair.

These summary statistics provide detailed information on the accuracy and precision of the data obtained for each concentration level. One objective of the statistical analysis of the data is to summarize the information about accuracy and precision which is contained in the statistics.

It is often the case that a systematic relationship exists between the mean recovery (X) and the true concentration level (C) of the analyte in the sample. In addition, there are often systematic relationships between the precision statistics (S and SR) and the mean recovery (X). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e., by a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a water type, and they can aid in comparing the behavior of the method across water types. In addition, they can be used to obtain estimates of the accuracy and precision at any concentration level within the applicable range studied. They can also be used to predict the behavior of the method when used under similar conditions. These important relationships are discussed below.

STATEMENT OF METHOD ACCURACY

The accuracy of the method is characterized by the relationship of the mean recovery (X) to the true concentration (C) of the analyte in the water

sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

$$X = a + b \cdot C \qquad (1)$$

was fitted to the data by regression techniques.

It is often the case that the true concentration values vary over a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least squares technique was used to fit the mean recovery data to the true concentration values. The weighted least square technique was performed by dividing both sides of Equation (1) by C resulting in Equation (2)

$$\frac{X}{C} = a \cdot \frac{1}{C} + b \qquad (2)$$

The {X/C} values were regressed against the {1/C} values using ordinary least squares to obtain estimates for the values of a and b. (This is equivalent to performing a weighted least squares with weights $w = 1/C^2$; see Reference 4, page 108 for details.) Equation (2) can easily be converted to the desired relationship given by Equation (1). The intercept (b) from Equation (2) becomes the slope (b) for Equation (1) and the slope (a) from Equation (2) becomes the intercept (a) for Equation (1). Equation (1) can be used to calculate the percent recovery over the applicable range of concentrations used in the study.

The percent recovery is given by

$$\text{Percent Recovery} = \left[\frac{a + b \cdot C}{C}\right] x\ 100 = \left[\frac{a}{C} + b\right] x\ 100 \qquad (3)$$

If the absolute value of the ratio (a/C) is small relative to the slope (b) for concentration in the low end of the range of concentration levels used in the study, then the percent recovery can be approximated by b x 100. For example, suppose the true concentration values range from 25 µg/L to 515 µg/L, the fitted line is given by $X = 0.20 + 0.85 \cdot C$. The percent recovery would be approximated by (0.85) x 100 = 85% over the specified range of 25 µg/L to 515 µg/L.

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If the ratio (a/C) is not small relative to the slope (b), then the percent recovery depends upon the true concentration (C), and it must be evaluated at each concentration value within the specified range.

STATEMENT OF METHOD PRECISION

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The precision of the method is characterized by the relationships between precision statistics (S and SR) and mean recovery (X). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot X \tag{4}$$

and

$$SR = f + g \cdot X^* \tag{5}$$

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were fitted to the data.

As discussed previously with respect to accuracy, the values of X and X* often vary over a wide range. In such cases, the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This will produce relatively larger errors in the estimates of S and SR at the lower mean recovery values. Therefore, a weighted least squares technique was also used to establish the values of the parameters d, e, f and g in Equations (4) and (5). The weighted least squares technique was performed by dividing both sides of Equation (4) by X* resulting in Equation (6)

$$\frac{S}{X} = d \cdot \frac{1}{X} + e \tag{6}$$

and by dividing both sides of Equation (5) by X* resulting in Equation (7)

$$\frac{SR}{X^*} = f \cdot \frac{1}{X^*} + g \tag{7}$$

The {S/X} values were regressed against the {1/X} values and the {SR/X*} values were regressed against the {1/X*} values using ordinary least squares to obtain estimates for the parameters d, e, f and g.

Equations (4) and (5) were obtained from Equations (6) and (7) in a manner similar to that discussed for mean recovery. The slope (d) for

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Equation (6) is the intercept (d) for Equation (4), and the intercept (e) for Equation (6) is the slope (e) for Equation (4). Similarly, the slope (f) for Equation (7) is the intercept (f) for Equation (5), and the intercept (g) for Equation (7) is the slope (g) for Equation (5).

Given Equations (4) and (5), the percent relative overall standard deviation and the percent relative single-analyst standard deviation are

$$\%RSD = \left[\frac{d}{X} + e\right] \times 100 \qquad (8)$$

and

$$\%RSD\text{-}SA = \left[\frac{f}{X^*} + g\right] \times 100 \qquad (9)$$

respectively. If the absolute value of the ratio (d/X) is small relative to the slope (e), then the percent relative overall standard deviation can be approximated by (e x 100) over the applicable range of mean recovery values. Similarly if the ratio (f/X*) is small relative to the slope (g), then the percent relative single-analyst standard deviation can be approximated by (g x 100) over the applicable range of mean recovery values.

If the ratios (d/X and f/X*) are not small relative to the slopes (e) and (f), then the percent relative standard deviations depend upon the values of the mean recovery statistics X and X*, and they should be evaluated separately for each value of X and X*.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 606 depend upon the type of water being analyzed. The summary statistics X, S and SR are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome since there are 36 mean recovery statistics (X) (six concentrations x six waters), 36 percent statistics (S) and 18 precision statistics (SR) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldly. Second, the statistical properties of this type of comparisons procedure are difficult to determine. Finally, due to

variation associated with X, S and SR, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may produce a significantly lower value than surface water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach, described in detail in Reference [7], has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is based on the following statistical model. If X_{ijk} denotes the measurement reported by laboratory i for water type j and ampule k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \quad . \qquad \begin{matrix} i = 1,2,\ldots,n \\ j = 1,2,\ldots,6 \\ k = 1,2,\ldots,6 \end{matrix} \qquad (10)$$

The model components β_j and γ_j are fixed parameters which determine the effect of water type j on the behavior the observed measurements $\{X_{ijk}\}$. The parameter C_k is the true concentration level associated with ampule k. The model component L_i is a random factor which accounts for the systematic error associated with laboratory i. The model component ε_{ijk} is the random factor which accounts for the within laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data $\{X_{ijk}\}$ and the true concentration level C_k through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight line models. Second, as will be seen below, there is an inherent increasing relationship between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements $\{X_{ijk}\}$. The expected value for the data modeled by Equation (10) is:

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \quad . \tag{11}$$

Precision is related to the variability in the measurements $\{X_{ijk}\}$. The variance of the data modeled by Equation (10) is

$$Var(X_{ijk}) = \left[\beta_j C_k^{\gamma_j}\right]^2 \; Var(L_i \cdot \varepsilon_{ijk}) \tag{12}$$

which is an increasing function of C_k. (See Reference [7] for a complete discussion of this model.)

The accuracy and precision of Method 606 depend upon water type through Equations (11) and (12) and the parameters $\{\beta_j\}$ and $\{\gamma_j\}$. If the $\{\beta_j\}$ and $\{\gamma_j\}$ vary with j (i.e., vary across water type), then the accuracy and precision of the method also vary across water type.

In order to determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation (10) represents the basic model. However, taking natural logarithms of both sides of Equation (10), the following straight line regression model is obtained,

$$\text{ℓn } X_{ijk} = \text{ℓn } \beta_j + \gamma_j \text{ ℓn } C_k + \text{ℓn } L_i + \text{ℓn } \varepsilon_{ijk} \tag{13}$$

which can be analyzed using standard linear model analysis techniques. The parameter ℓn β_j is the intercept and γ_j the slope of the regression line associated with water type j. It is assumed that ℓn L_i is normally distributed with mean 0 and variance σ_ζ^2 and that ℓn ε_{ijk} is normally distributed with mean 0 and variance σ_ε^2 and that the $\{\text{ℓn } L_i\}$ and $\{\text{ℓn } \varepsilon_{ijk}\}$ terms are independent.

Based on Equation (13) the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameters ℓn β_j (and hence β_j) and γ_j can be estimated. The estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative statistical hypotheses H_0 and H_A are given by

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H_0: $\ln \beta_j - \ln \beta_1 = 0$ and $\gamma_j - \gamma_1 = 0$ for $j = 2,3,4,5,6$

versus

H_A: $\ln \beta_j - \ln \beta_1 \neq 0$ and/or $\gamma_j - \gamma_1 \neq 0$ for some $j = 2,3,4,5,6$

The test of null hypothesis H_0 against the alternative hypothesis H_A is based on an F-statistic derived from standard linear model theory. The probability of obtaining a value of an F-statistic as large as the value which was actually observed (F OBS), denoted by P(F > F OBS), is calculated under the assumption that H_0 is true. The null hypothesis H_0 is rejected in favor of H_A if P(F > F OBS) is less than 0.05.

If H_0 is rejected, then some linear combination of the differences $\ln \beta_j - \ln \beta_1$ and $\gamma_j - \gamma_1$ is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to minor systematic effect common to several water types. The effect due to a specific water type is judged to be statistically significant only if one of the differences $\ln \beta_j - \ln \beta_1$ and/or $\gamma_j - \gamma_1$ is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences $\ln \beta_j - \ln \beta_1$ or $\gamma_j - \gamma_1$ fails to include zero, then the statistical significance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the difference.

The interpretation of the differences involves comparing the mean recovery and standard deviation of the $\{X_{ijk}\}$ data for each water type to the mean recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type j is given by Equation (11). The mean recovery for water type j is compared to that for distilled water (j=1) on a relative basis by

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$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j \, C_k^{\gamma_j} \, E(L_i \cdot \varepsilon_{ijk})}{\beta_1 \, C_k^{\gamma_1} \, E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1} \, C_k^{\gamma_j - \gamma_1} \qquad (14)$$

[The ratio of the standard deviations would be equivalent to Equation (14) and therefore the interpretation of the effect on precision is the same as that for the effect on mean recovery.]

The ratio in Equation (14) is a measure of the relative difference in mean recovery between water type j and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e., the constant bias) and (b) $C_k^{\gamma j - \gamma i}$ which depends upon the true concentration level (i.e., the concentration dependent bias). If $\gamma_j - \gamma_1$ is zero, then the relative difference in mean recovery is just β_j/β_1 which is independent of concentration level C_k. It can then be stated that the mean recovery of water type j is (β_j/β_1) x 100% of the mean recovery for distilled water. If $\gamma_j - \gamma_1$ is not zero, then the mean recovery of water type j is $[(\beta_j/\beta_1) \cdot C_k^{\gamma j - \gamma 1})$ x 100% of that for distilled water and therefore depends upon the true concentration level C_k.

In order to illustrate these points consider the following example. Suppose that a significant F-value has been obtained and the confidence intervals for all the differences contain zero except for water type 5. For water type 5, the point estimate for $\ell n\, \beta_5 - \ell n\, \beta_1$ is -0.38 and the confidence interval for $\ell n\, \beta_5 - \ell n\, \beta_1$ is (-0.69, -0.07). The point estimate for $\gamma_5 - \gamma_1$ is 0.07, and the confidence interval for $\gamma_5 - \gamma_1$ is (-0.04, 0.18). In this case a statistically significant effect due to water type has been established which involves only water type 5. The practical significance of this effect is judged by considering Equation (14). The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{i5k})}{E(X_{i1k})} = \frac{\beta_5}{\beta_1} \, C_k^{\gamma_5 - \gamma_1} \qquad (15)$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{ijk})}{Var(X_{i1k})}} = \frac{\beta_5}{\beta_1} \, C_k^{\gamma_5 - \gamma_1} \qquad (16)$$

Since the confidence interval for $\gamma_5 - \gamma_1$ contains zero this difference is assumed to be insignificant and is set to zero. Therefore, Equations (15) and (16) reduce to β_5/β_1. The point estimate for $\ell n\, \beta_5 - \ell n\, \beta_1$ was -0.38.

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Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68% of the mean recovery for distilled water. Similarly the standard deviation for the data for water type 5 is estimated to be 68% of the standard deviation for distilled water. Since the 95% confidence interval for $\ell n\ \beta_5 - \ell n\ \beta_1$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50% to 93% of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend upon the importance of a mean recovery (standard deviation) which is between 50% and 93% of the mean recovery (standard deviation) observed for distilled water.

The comparison of accuracy and precision across water types just discussed is based on the assumption that Equation (10) approximately models the data. It is clear that in practical monitoring programs of this type such models cannot model the data completely in every case. This analysis, therefore, is viewed as a screening procedure which identifies those cases where differences in water types are likely to be present. A more detailed, local analysis can then be pursued using the basic summary statistics for precision and accuracy.

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SECTION 5

DISCUSSION AND CONCLUSIONS

There was a high rejection ratio for the data submitted on this study, ranging from 15% of the DBP to 29% of the DEP results. These rejections include missing data, data reported as less than some value, the rejection of one laboratory in entirety, and statistical outliers rejected according to the criteria stated earlier. Overall, 748 values were not included or 21.6% of all data requested.

The summary statistics obtained from the collaborative study data are presented in Tables 3 through 8 for the six phthalate esters studied. Discussion of the accuracy, precision, and consistency across water types is presented separately in the following sections.

ACCURACY OF THE METHOD

The accuracy of the method is presented in terms of linear regression equations between the true dosing level and the mean recovered amount. The recovery that can be expected for the six phthalates under study is illustrated in Table 9. For this example, the midranges of the concentrations used in this study were inserted into the regression equations and the predicted concentration expressed as a percentage of the midrange. These predicted recoveries at the midrange provide a basis for comparing the recoveries across wastewaters and among phthalates. Recoveries at other concentrations would vary due to the relative impact of the slope and the intercept of the regression line upon the calculated result.

Overall there is good consistency among the recoveries for a particular phthalate across water types. The primary exceptions to this are the wide range of recoveries of bis-2-ethylhexyl phthalate in the various water types and the low recovery for DOP in the laboratory pure water.

PRECISION OF THE METHOD

The precision of the method is estimated by calculating regression equations for the precision components versus the mean recovery. In each

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TABLE 3

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

STATISTICAL SUMMARY FOR DIMETHYL PHTHALATE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
NUMBER OF DATA POINTS	12	11	12	12	11	12	10	10	8	10	9	9
TRUE VALUE UG/L	1.75	2.24	1.75	2.24	1.75	2.24	1.75	2.24	1.75	2.24	1.75	2.24
MEAN RECOVERY	1.28	2.09	1.44	1.75	1.49	2.40	1.37	1.92	1.02	1.45	1.52	1.56
ACCURACY AS % REL ERROR	-26.72	-6.70	-17.79	-21.97	-14.85	6.99	-21.46	-14.50	-41.96	-35.22	-13.26	-30.27
OVERALL STD DEV (S)	.86	1.25	.71	1.14	.76	1.38	.56	.86	.53	.95	1.18	1.07
OVERALL REL STD DEV, %	67.21	59.56	49.54	65.36	51.00	57.53	40.81	45.09	52.47	65.14	77.54	68.31
SINGLE STD DEV, (SR)	.57		.78		.65		.54		.44		1.00	
ANALYST REL DEV, %	33.70		48.85		33.28		32.69		38.65		64.65	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
NUMBER OF DATA POINTS	12	12	12	11	12	13	11	10	12	12	10	11
TRUE VALUE UG/L	9.60	12.30	9.60	12.30	9.60	12.30	9.60	12.30	9.60	12.30	9.60	12.30
MEAN RECOVERY	7.34	10.46	7.52	12.51	6.79	10.67	6.94	7.63	6.30	9.37	8.43	8.49
ACCURACY AS % REL ERROR	-23.50	-14.96	-21.62	1.69	-29.43	-13.25	-27.73	-37.99	-34.33	-23.80	-12.54	-30.95
OVERALL STD DEV (S)	3.75	5.11	2.18	8.20	1.39	5.53	3.15	3.56	.92	3.39	3.92	4.04
OVERALL REL STD DEV, %	51.12	58.40	28.98	65.59	20.45	51.82	45.45	46.62	14.58	36.14	46.66	47.61
SINGLE STD DEV, (SR)	2.46		3.69		3.53		1.85		2.07		2.96	
ANALYST REL DEV, %	27.59		36.81		40.45		25.45		26.43		35.07	
HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	12	12	12	13	13	13	11	11	11	12	12	11
TRUE VALUE UG/L	21.00	26.90	21.00	26.90	21.00	26.90	21.00	26.90	21.00	26.90	21.00	26.90
MEAN RECOVERY	13.97	18.39	14.02	22.02	14.25	18.99	13.41	19.33	14.86	19.42	12.97	18.35
ACCURACY AS % REL ERROR	-33.46	-31.63	-23.73	-14.13	-32.16	-29.76	-36.16	-28.13	-29.26	-27.82	-39.73	-31.78
OVERALL STD DEV (S)	5.20	7.58	5.04	10.22	5.40	8.41	5.49	6.56	5.67	7.99	6.85	8.12
OVERALL REL STD DEV, %	37.23	41.23	37.73	46.43	37.87	44.52	40.98	33.95	38.17	41.13	53.21	44.23
SINGLE STD DEV, (SR)	4.22		5.43		5.07		5.09		5.10		4.44	
ANALYST REL DEV, %	26.10		28.57		30.58		31.09		29.76		28.43	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE 4

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

STATISTICAL SUMMARY FOR DI-N-BUTYLPHTHALATE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
NUMBER OF DATA POINTS	14	13	13	13	14	14	14	13	14	14	12	13
TRUE VALUE UG/L	3.49	2.48	3.49	2.48	3.49	2.48	3.49	2.48	3.49	2.48	3.49	2.48
MEAN RECOVERY	2.74	2.20	2.96	2.16	3.00	2.41	2.71	2.28	3.12	2.07	2.69	2.06
ACCURACY AS % REL ERROR	-21.41	-11.41	-15.27	-12.75	-14.00	-2.82	-22.45	-8.13	-10.55	-16.42	-22.98	-16.98
OVERALL STD DEV (S)	.80	.91	1.37	.64	1.22	1.03	1.01	1.06	2.10	.98	1.09	1.00
OVERALL REL STD DEV, %	29.30	35.78	46.19	29.78	40.80	42.88	37.29	46.63	67.37	47.16	40.50	48.61
SINGLE ANALYST STD DEV, (SR)	.78		.89		.79		.54		1.59		.52	
SINGLE ANALYST REL DEV, %	31.59		34.73		28.74		21.83		60.92		21.75	

MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
NUMBER OF DATA POINTS	14	13	12	10	14	14	14	13	14	15	14	14
TRUE VALUE UG/L	14.00	9.90	14.00	9.90	14.00	9.90	14.00	9.90	14.00	9.90	14.00	9.90
MEAN RECOVERY	11.09	8.33	10.57	8.42	11.54	7.78	11.17	7.53	12.73	8.75	10.95	9.02
ACCURACY AS % REL ERROR	-20.76	-15.83	-24.47	-14.95	-17.54	-21.41	-20.21	-24.28	-9.10	-11.59	-21.76	-8.85
OVERALL STD DEV (S)	2.35	1.62	2.92	1.99	3.18	2.43	4.98	1.53	4.51	3.07	3.33	4.77
OVERALL REL STD DEV, %	21.16	19.42	27.59	23.57	44.89	31.29	44.60	20.40	35.45	35.05	30.44	52.83
SINGLE ANALYST STD DEV, (SR)	1.92		1.86		3.20		3.06		2.99		3.13	
SINGLE ANALYST REL DEV, %	19.78		19.53		33.10		32.81		27.88		31.33	

HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	14	14	12	14	15	15	14	14	15	15	14	13
TRUE VALUE UG/L	34.90	24.80	34.90	24.80	34.90	24.80	34.90	24.80	34.90	24.80	34.90	24.80
MEAN RECOVERY	25.85	20.86	23.69	19.71	26.50	21.49	24.51	19.70	26.69	20.60	24.94	19.35
ACCURACY AS % REL ERROR	-25.94	-15.88	-32.13	-20.54	-24.08	-13.37	-29.78	-20.57	-23.52	-16.93	-28.53	-21.97
OVERALL STD DEV (S)	10.96	7.07	6.60	5.44	7.53	5.98	10.27	4.99	8.76	6.52	8.72	9.68
OVERALL REL STD DEV, %	42.42	33.99	27.85	32.70	28.30	27.81	41.90	25.13	32.84	31.67	34.96	29.37
SINGLE ANALYST STD DEV, (SR)	6.45		5.44		6.97		7.04		5.61		5.11	
SINGLE ANALYST REL DEV, %	27.62		25.09		29.04		31.84		23.72		23.09	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE 5

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

STATISTICAL SUMMARY FOR DIETHYLPHTHALATE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
NUMBER OF DATA POINTS	12	12	13	13	13	11	13	11	9	11	8	8
TRUE VALUE UG/L	2.11	1.70	2.11	1.70	2.11	1.70	2.11	1.70	2.11	1.70	2.11	1.70
MEAN RECOVERY	1.39	1.45	2.12	1.27	2.23	1.29	2.48	1.57	1.03	1.47	1.35	1.35
ACCURACY AS % REL ERROR	-34.10	-14.68	.44	-25.23	5.76	-24.18	17.72	-7.42	-51.07	-13.72	-35.94	-20.79
OVERALL STD DEV (S)	.76	.71	1.00	.56	1.85	.87	1.92	1.17	.66	1.24	1.00	.82
OVERALL REL STD DEV, %	54.99	48.74	47.18	44.01	82.79	67.62	77.26	74.14	63.52	84.42	74.12	60.65
SINGLE STD DEV, (SR)	.42		.52		.60		.69		.46		.35	
ANALYST REL DEV, %	29.65		30.79		34.14		34.24		36.95		25.73	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
NUMBER OF DATA POINTS	13	14	13	10	12	14	13	14	13	13	12	12
TRUE VALUE UG/L	12.60	10.20	12.60	10.20	12.60	10.20	12.60	10.20	12.60	10.20	12.60	10.20
MEAN RECOVERY	9.00	8.97	9.71	9.04	8.62	8.86	9.11	12.05	9.30	8.88	10.78	10.59
ACCURACY AS % REL ERROR	-36.51	-12.11	-22.92	-11.33	-31.61	-13.10	-27.68	18.12	-26.19	-12.96	-14.48	3.82
OVERALL STD DEV (S)	3.46	5.31	4.63	2.36	3.27	4.68	4.88	9.27	4.49	3.69	8.45	7.79
OVERALL REL STD DEV, %	43.27	59.27	47.64	26.06	37.89	52.82	53.59	76.94	48.26	41.60	78.39	73.54
SINGLE STD DEV, (SR)	2.81		2.71		2.82		4.25		3.15		6.21	
ANALYST REL DEV, %	33.17		28.91		32.31		40.12		34.61		58.15	
HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	14	14	12	13	14	14	14	14	12	13	12	12
TRUE VALUE UG/L	27.40	22.20	27.40	22.20	27.40	22.20	27.40	22.20	27.40	22.20	27.40	22.20
MEAN RECOVERY	18.50	15.26	16.65	14.73	21.58	16.78	22.06	17.58	19.72	17.28	22.87	16.37
ACCURACY AS % REL ERROR	-32.47	-31.26	-39.22	-33.64	-21.24	-24.40	-19.48	-20.83	-28.03	-22.15	-16.53	-26.27
OVERALL STD DEV (S)	7.51	6.28	8.18	5.70	8.97	7.24	12.39	8.07	11.32	7.98	13.12	9.19
OVERALL REL STD DEV, %	40.60	41.15	49.13	38.72	41.55	43.12	56.18	45.91	57.41	46.15	57.35	56.17
SINGLE STD DEV, (SR)	3.65		4.36		4.39		7.23		5.44		6.96	
ANALYST REL DEV, %	21.64		27.79		22.88		36.50		29.49		35.49	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE 6

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

STATISTICAL SUMMARY FOR BUTYLBENZYLPHTHALATE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
NUMBER OF DATA POINTS	12	12	12	13	13	12	11	11	12	10	12	11
TRUE VALUE UG/L	0.70	0.87	0.70	0.87	0.70	0.87	0.70	0.87	0.70	0.87	0.70	0.87
MEAN RECOVERY	.68	.89	.74	.82	.77	1.14	.65	.70	.70	.89	.67	.84
ACCURACY AS % REL ERROR	-2.45	2.38	5.21	-5.74	9.96	31.49	-7.60	-19.25	-.14	1.75	-4.90	-3.97
OVERALL STD DEV (S)	.20	.38	.26	.30	.34	.33	.26	.36	.35	.35	.25	.29
OVERALL REL STD DEV, %	29.69	42.25	35.97	35.65	43.97	28.57	40.19	51.71	49.95	40.10	35.90	35.21
SINGLE STD DEV, (SR)	.25		.21		.20		.29		.15		.19	
ANALYST REL DEV, %	31.24		27.62		20.95		43.09		18.48		25.69	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
NUMBER OF DATA POINTS	12	11	13	11	11	14	13	11	13	13	12	13
TRUE VALUE UG/L	4.18	5.23	4.18	5.23	4.18	5.23	4.18	5.23	4.18	5.23	4.18	5.23
MEAN RECOVERY	3.66	4.32	3.87	5.15	4.16	6.04	3.55	4.47	3.69	4.56	3.22	5.52
ACCURACY AS % REL ERROR	-12.36	-17.33	-7.43	17.76	-.41	15.41	-15.07	-14.53	-11.43	-12.87	-23.01	5.55
OVERALL STD DEV (S)	.53	1.24	.92	2.76	.50	3.40	1.74	.98	.51	1.60	.81	2.60
OVERALL REL STD DEV, %	14.36	28.77	23.83	44.88	11.93	56.29	48.96	21.88	13.80	35.07	25.28	47.07
SINGLE STD DEV, (SR)	1.13		1.94		1.65		1.18		1.02		1.43	
ANALYST REL DEV, %	28.42		38.64		32.45		29.42		24.62		32.64	
HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	12	12	13	13	12	13	12	12	13	13	12	12
TRUE VALUE UG/L	9.75	12.20	9.75	12.20	9.75	12.20	9.75	12.20	9.75	12.20	9.75	12.20
MEAN RECOVERY	7.90	10.32	8.27	9.77	8.58	10.01	7.31	9.37	8.09	10.69	7.36	9.77
ACCURACY AS % REL ERROR	-18.96	-15.45	-15.22	-19.92	-12.04	-17.93	-25.01	-23.21	-16.99	-12.36	-24.50	-19.92
OVERALL STD DEV (S)	2.35	3.01	3.58	3.44	2.51	2.66	2.61	3.29	2.47	2.50	1.66	2.20
OVERALL REL STD DEV, %	29.89	29.20	43.35	35.20	30.49	26.61	35.72	35.12	30.54	23.40	22.92	22.50
SINGLE STD DEV, (SR)	2.37		2.21		2.62		2.09		2.35		1.83	
ANALYST REL DEV, %	25.98		24.46		28.22		25.03		25.02		21.41	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 7

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

STATISTICAL SUMMARY FOR BIS-2-ETHYLHEXYLPHTHALATE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
NUMBER OF DATA POINTS	10	9	11	14	11	11	12	12	12	12	10	13
TRUE VALUE UG/L	5.07	6.95	5.07	6.95	5.07	6.95	5.07	6.95	5.07	6.95	5.07	6.95
MEAN RECOVERY	4.53	6.11	4.35	9.04	10.13	9.76	7.66	6.18	3.98	14.04	14.27	14.14
ACCURACY AS % REL ERROR	-10.75	-12.12	-14.22	30.10	99.87	40.46	51.04	-11.13	-21.48	102.05	181.42	103.53
OVERALL STD DEV (S)	3.04	4.48	2.57	9.29	8.81	7.77	10.53	5.27	1.62	13.54	15.50	17.19
OVERALL REL STD DEV, %	67.10	73.32	59.11	91.62	86.98	79.63	137.46	85.40	40.59	96.42	108.60	121.58
SINGLE ANALYST STD DEV, (SR)	1.85		2.88		9.60		7.89		8.42		14.79	
SINGLE ANALYST REL DEV, %	34.74		42.62		96.49		114.05		93.40		104.09	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
NUMBER OF DATA POINTS	12	14	12	12	10	12	14	13	13	14	14	13
TRUE VALUE UG/L	23.30	27.80	20.30	27.80	20.30	27.80	20.30	27.80	20.30	27.80	20.30	27.80
MEAN RECOVERY	11.34	15.50	14.12	25.77	14.70	22.96	16.95	26.44	18.70	20.43	21.13	21.97
ACCURACY AS % REL ERROR	-44.15	-44.23	-30.44	-3.70	-27.59	-17.40	-16.48	-4.53	-7.87	-26.50	4.09	-20.97
OVERALL STD DEV (S)	8.25	13.58	6.09	12.75	9.53	11.92	10.21	14.81	12.96	9.79	17.70	9.52
OVERALL REL STD DEV, %	72.74	84.23	43.12	47.61	64.80	51.89	60.24	55.80	69.28	47.90	83.78	43.35
SINGLE ANALYST STD DEV, (SR)	7.13		8.18		9.91		11.46		9.61		12.03	
SINGLE ANALYST REL DEV, %	53.17		40.02		52.61		52.70		49.11		55.83	
HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	13	14	14	14	13	13	13	12	14	14	15	15
TRUE VALUE UG/L	40.60	55.60	40.60	55.60	40.60	55.60	40.60	55.60	40.60	55.60	40.60	55.60
MEAN RECOVERY	27.35	30.06	29.78	37.21	28.95	36.85	33.79	34.72	37.60	40.50	31.91	41.86
ACCURACY AS % REL ERROR	-32.64	-45.94	-26.65	-33.07	-28.69	-33.72	-16.79	-37.55	-7.40	-27.16	-21.41	-24.72
OVERALL STD DEV (S)	20.05	21.74	12.41	19.24	11.56	15.13	18.68	18.09	23.41	15.32	11.79	17.81
OVERALL REL STD DEV, %	73.33	72.34	41.67	51.70	40.27	41.05	55.30	52.10	62.28	37.83	36.94	42.55
SINGLE ANALYST STD DEV, (SR)	22.31		12.03		9.14		10.14		17.31		10.15	
SINGLE ANALYST REL DEV, %	77.74		35.92		27.79		29.59		44.33		27.51	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE 8

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

STATISTICAL SUMMARY FOR DI-N-OCTYLPHTHALATE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
NUMBER OF DATA POINTS	13	11	15	15	13	13	12	10	12	13	12	11
TRUE VALUE UG/L	17.70	14.10	17.70	14.10	17.70	14.10	17.70	14.10	17.70	14.10	17.70	14.10
MEAN RECOVERY	5.55	4.26	15.41	10.53	10.25	10.02	10.51	8.77	10.60	7.74	7.62	7.56
ACCURACY AS % REL ERROR	-68.65	-69.82	-12.92	-25.34	-42.12	-28.96	-40.65	-37.83	-40.13	-45.13	-56.93	-46.41
OVERALL STD DEV (S)	4.36	2.65	9.01	5.77	4.43	3.36	4.08	3.36	5.53	3.17	3.82	3.79
OVERALL REL STD DEV, %	78.54	62.25	58.44	54.79	43.22	33.57	38.86	38.37	52.22	40.92	50.09	50.13
SINGLE ANALYST STD DEV, (SR)	2.58		7.91		2.09		2.38		2.69		4.22	
SINGLE ANALYST REL DEV, %	52.72		60.99		20.04		24.67		29.32		55.54	

MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
NUMBER OF DATA POINTS	12	13	15	12	13	14	13	13	14	14	12	12
TRUE VALUE UG/L	70.70	56.30	70.70	56.30	70.70	56.30	70.70	56.30	70.70	56.30	70.70	56.30
MEAN RECOVERY	23.81	18.60	60.87	46.55	49.52	41.03	46.30	40.90	48.24	33.42	37.66	33.90
ACCURACY AS % REL ERROR	-66.32	-66.96	-13.91	-17.32	-29.96	-27.13	-34.51	-27.35	-31.76	-40.64	-46.73	-39.79
OVERALL STD DEV (S)	16.08	12.69	26.48	12.32	20.98	18.53	19.22	15.27	16.18	15.27	19.23	12.77
OVERALL REL STD DEV, %	67.55	68.22	43.51	26.47	42.38	45.16	41.52	37.35	33.54	45.69	51.05	37.65
SINGLE ANALYST STD DEV, (SR)	8.79		22.93		10.99		10.73		13.66		14.69	
SINGLE ANALYST REL DEV, %	41.46		42.69		24.27		24.61		33.46		41.07	

HIGH YOUDEN PAIR	2	4	2	6	2	6	2	6	2	6	2	6
NUMBER OF DATA POINTS	13	13	14	15	14	14	13	13	14	14	13	13
TRUE VALUE UG/L	106.00	84.50	106.00	84.50	106.00	84.50	106.00	84.50	106.00	84.50	106.00	84.50
MEAN RECOVERY	37.58	29.30	74.23	59.03	73.81	52.90	68.01	43.85	68.24	53.93	62.83	50.58
ACCURACY AS % REL ERROR	-64.54	-65.32	-29.97	-30.15	-30.37	-37.40	-35.84	-48.11	-35.63	-36.18	-40.73	-40.15
OVERALL STD DEV (S)	20.54	18.31	40.54	31.73	27.86	17.56	28.11	23.03	27.63	15.05	22.40	16.85
OVERALL REL STD DEV, %	54.66	62.48	54.62	53.76	37.74	33.19	41.33	52.52	40.49	27.91	35.65	33.32
SINGLE ANALYST STD DEV, (SR)	13.52		10.58		16.39		17.92		11.53		8.35	
SINGLE ANALYST REL DEV, %	40.44		15.88		25.87		32.04		18.88		14.73	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE 9. ESTIMATED PERCENT RECOVERY FOR VARIOUS WATER TYPES

Compound	Percent recovery in given water types						
	Midrange	Laboratory pure	Finished drinking	Surface	Industrial effluent 1	Industrial effluent 2	Industrial effluent 3
dimethyl phthalate	14.3	74	84	75	68	75	71
diethyl phthalate	14.55	71	74	79	88	76	85
di-n-butyl phthalate	18.69	80	77	80	76	84	79
butylbenzyl phthalate	6.45	80	93	96	80	87	85
bis-2-ethylhexyl phthalate	30.065	60	80	74	79	90	85
di-n-octylphthalate	30.295	33	78	67	63	61	55

case, the overall standard deviation (S) and single-analyst standard deviation (SR) have been expressed in terms of relative standard deviations at the midrange concentration for illustration purposes.

The percent relative deviations are given in Table 10 for the overall standard deviation and in Table 11 for the single-analyst standard deviation. These percent relative standard deviations are not consistent across water types in several instances, and some of the values require some explanation. Three slopes of the regression equations had a negative value, those for overall standard deviations for 2EHP in industrial effluent 3 and for single-analyst in surface and industrial effluent 3 for 2EHP. In these cases, there was a significant intercept and standard deviations were roughly equivalent over the range studied. Thus, the percent relative standard deviation would vary relative to the change in concentration.

Also of interest to the evaluation of these data for two of the six phthalates, the 2EHP and DOP, the largest relative standard deviations at the midrange were observed in the laboratory pure water. This apparently stems from difficulty in obtaining a consistent laboratory blank value.

COMPARISON ACROSS WATER TYPES

The summaries on the effects of water type on the results obtained are presented in Tables 12 through 17. The only significant effects, i.e., a nonzero difference between a test water and the laboratory pure water, were found for DOP in the finished drinking, surface and industrial effluent 1. In these instances, a positive difference was detected between the intercepts of the regression lines. This translates to a difference in the average percent recovery of the method in these water types. As can be seen from Table 9, this resulted from the low recovery observed for DOP in the laboratory pure water.

This low average recovery was unexpected based on the method development work. However, the water used in that study was a natural water that was low in organics but relatively high in inorganic salts (hardness as $CaCO_3$ greater than 200 ppm) which could have exerted a salting out effect resulting in higher recoveries than would be observed in laboratory pure water. The recoveries from the five test waters were reasonably consistent, with regression slopes of 0.60 to 0.76 and midrange recoveries from 55 to 78%.

Although no other differences were noted, it should be taken into consideration that this study was conducted with three industrial effluents

TABLE 10. ESTIMATED OVERALL PERCENT RELATIVE STANDARD DEVIATION FOR VARIOUS WATER TYPES AT MIDRANGE CONCENTRATION

	Overall RSD for given water type						
Compound	Midrange	Laboratory pure	Finished drinking	Surface	Industrial effluent 1	Industrial effluent 2	Industrial effluent 3
dimethyl phthalate	14.3	46	45	40	41	33	47
diethyl phthalate	14.55	46	40	45	58	50	66
di-n-butyl phthalate	18.69	29	29	33	33	35	35
butylbenzyl phthalate	6.45	24	37	31	35	26	29
bis-2-ethylhexyl phthalate	30.065	74	51	44	56	62	47
di-n-octyl phthalate	30.295	63	48	40	46	39	40

TABLE 11. ESTIMATED SINGLE-ANALYST PERCENT RELATIVE STANDARD DEVIATION FOR VARIOUS WATER TYPES AT MIDRANGE CONCENTRATION

	Single-analyst RSD for given water type						
Compound	Midrange	Laboratory pure	Finished drinking	Surface	Industrial effluent 1	Industrial effluent 2	Industrial effluent 3
dimethyl phthalate	14.3	27	32	35	28	28	30
diethyl phthalate	14.55	27	28	27	38	31	49
di-n-butyl phthalate	18.69	24	22	31	33	24	27
butylbenzyl phthalate	6.45	27	32	30	27	25	27
bis-2-ethylhexyl phthalate	30.065	72	38	31	38	44	36
di-n-octyl phthalate	30.295	40	38	24	27	27	30

TABLE 12

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

EFFECT OF WATER TYPE ON DIETHYLPHTHALATE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .96105

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.1568	-.0401
3	-.0616	.0579
4	.1199	-.0158
5	-.2771	.1157
6	-.0842	.0637

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	473.93511	473.93511		
REG(WATER/DISTILLED)	10	2.13710	.21071	.62	.7942
ERROR	419	141.63476	.33803		
TOTAL	430	617.67696			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.1568	(-.4245 , .7381)	-.0401	(-.2863 , .2060)
3	-.0616	(-.6533 , .5301)	.0579	(-.1895 , .3052)
4	.1199	(-.4719 , .7116)	-.0158	(-.2629 , .2312)
5	-.2771	(-.8949 , .3406)	.1157	(-.1410 , .3723)
6	-.0842	(-.7419 , .5733)	.0637	(-.2055 , .3329)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

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TABLE 13

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

EFFECT OF WATER TYPE ON DIMETHYL PHTHALATE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .98353

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0381	.0575
3	.2397	-.0649
4	.1690	-.0501
5	-.2677	.1041
6	-.1690	.0483

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	422.43789	422.43789		
REG(WATER/DISTILLED)	10	3.04478	.30448	1.32	.2193
ERROR	382	88.34228	.23126		
TOTAL	393	513.82495			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	-.0381	(-.5440 , .4677)	.0575	(-.1588 , .2737)
3	.2397	(-.2715 , .7509)	-.0649	(-.2817 , .1520)
4	.1690	(-.3613 , .6993)	-.0501	(-.2756 , .1753)
5	-.2677	(-.8129 , .2774)	.1041	(-.1246 , .3329)
6	-.1690	(-.7136 , .3757)	.0483	(-.1807 , .2773)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

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TABLE 14

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

EFFECT OF WATER TYPE ON DI-N-BUTYLPHTHALATE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .95724

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	-.0099	-.0075
3	-.0158	.0033
4	-.0534	-.0074
5	-.2086	.0665
6	-.1003	.0229

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	428.23592	428.23592		
REG(WATER/DISTILLED)	10	.62857	.06286	.43	.9300
ERROR	465	67.41165	.14497		
TOTAL	476	496.27614			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL		SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL	
2	-.0099	(-.4534 ,	.4336)	-.0075	(-.1842 ,	.1692)
3	-.0158	(-.4489 ,	.4172)	.0033	(-.1683 ,	.1750)
4	-.0534	(-.4915 ,	.3847)	-.0074	(-.1814 ,	.1665)
5	-.2086	(-.6415 ,	.2243)	.0665	(-.1051 ,	.2381)
6	-.1003	(-.5438 ,	.3432)	.0229	(-.1529 ,	.1987)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

TABLE 15

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

EFFECT OF WATER TYPE ON BUTYLBENZYLPHTHALATE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .94386

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0482	-.0043
3	.2001	-.0550
4	-.2306	.0760
5	-.0361	.0375
6	-.0059	.0113

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	477.77051	477.77051		
REG(WATER/DISTILLED)	10	3.47706	.34771	1.92	.0404
ERROR	411	74.26164	.18059		
TOTAL	422	555.50921			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.0482	(-.2476 , .3440)	-.0043	(-.1830 , .1743)
3	.2001	(-.0952 , .4954)	-.0550	(-.2332 , .1231)
4	-.2306	(-.5361 , .0748)	.0760	(-.1068 , .2588)
5	-.0361	(-.3397 , .2676)	.0375	(-.1436 , .2186)
6	-.0059	(-.3075 , .2957)	.0113	(-.1698 , .1925)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

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TABLE 16

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SPI PHTHALATE EST

EFFECT OF WATER TYPE ON BIS-2-ETHYLHEXYLPHTHALATE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .76093

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.1123	.0959
3	.8288	-.0971
4	-.2392	.2035
5	.2879	.0637
6	.7578	-.0669

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	209.99572	209.99572		
REG(WATER/DISTILLED)	10	18.75054	1.87505	4.22	.0000
ERROR	428	190.16252	.44430		
TOTAL	439	418.90878			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	.1123	(-1.0143 , 1.2389)	.0959	(-.2628 , .4546)
3	.8288	(-.3221 , 1.9797)	-.0971	(-.4628 , .2686)
4	-.2392	(-1.3762 , .8978)	.2035	(-.1598 , .5668)
5	.2879	(-.8418 , 1.4176)	.0637	(-.2950 , .4224)
6	.7579	(-.3954 , 1.9010)	-.0669	(-.4278 , .2940)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

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TABLE 17

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

EFFECT OF WATER TYPE ON DI-N-OCTYLPHTHALATE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = 1.21807

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	1.9886	-.2719
3	1.6142	-.1912
4	1.6543	-.2320
5	1.2379	-.1182
6	.9278	-.0604

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	313.85353	313.85353		
REG(WATER/DISTILLED)	10	46.89344	4.68934	16.16	.0000
ERROR	444	128.84682	.29020		
TOTAL	455	489.59379			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	INTERVAL
2	1.9886	(.7816 , 3.1955)	-.2719	(-.5810 , .0372)
3	1.6142	(.3734 , 2.8549)	-.1912	(-.5078 , .1254)
4	1.6543	(.3631 , 2.9454)	-.2320	(-.5600 , .0960)
5	1.2379	(-.0098 , 2.4857)	-.1182	(-.4360 , .1996)
6	.9278	(-.3493 , 2.2049)	-.0604	(-.3858 , .2650)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

FOR COMPLETE DETAILS ON INTERPRETING THIS REPORT, SEE APPENDIX A IN THE PROGRAMMER(S) DOCUMENTATION.

that were intentionally selected to provide a low background of potentially interfering compounds. Some inconsistency was noted from one matrix to another in the summary data, though not enough to produce statistical significance. The analyst should not necessarily expect to obtain the results presented here when analyzing for phthalate esters in differing effluents.

METHOD EVALUATION

The accuracy of the method as determined from the collaborative study data can be compared to the results obtained in the development study on the methodology. In the wastewater application phase of that program, data were obtained from three wastewaters for DMP and DEP and four wastewaters for the remainder. The DMP recoveries in the development ranged from 88 to 100% and the DEP from 82 to 100%, somewhat higher than observed in the interlaboratory study. Recoveries for the other phthalates in the two studies were more comparable with recoveries of 50 to 80% the norm. Spike levels for DMP and DEP were generally higher in the previous work than in the method study, which may account for some of the difference in recovery. There were notable differences in the recoveries obtained from different effluents in the previous work as well.

In a separate study, method detection limit (MDL) was determined for each of the six compounds in interference-free water and in two industrial effluents, using a procedure specified by the Environmental Monitoring and Support Laboratory. In this procedure, at least seven sample replicates containing the compounds at concentrations near the estimated detection limit of each were analyzed by Method 606. The standard deviation of the replicate measurements were calculated and multiplied by the Student's t value appropriate for a 99% confidence level with n-1 degrees of freedom (3.143 for seven replicates) to give the MDL value. The MDL values obtained are given in Table 18. Also shown in Table 18 for easy comparison with the MDLs are the lowest concentrations used in the interlaboratory study.

TABLE 18. METHOD DETECTION LIMITS AND LOWEST CONCENTRATIONS USED IN STUDY

	Concentration, µg/L					
	DMP	DEP	DBP	BBP	2EHP	DOP
Interference-free water, MDL	0.286	0.493	0.358	0.343	1.95	3.02
Industrial effluent 1, MDL	0.842	0.666	1.02	0.666	4.23	8.18
Industrial effluent 3, MDL	0.770	1.25	1.14	0.231	3.99	8.75
Lowest conc. in study	1.746	1.695	2.475	0.696	5.071	14.083

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In conjunction with the MDL determinations, analytical curves for the compounds were determined on duplicate samples at five concentration levels chosen in conference with the project officer. The analytical curves for these substances showed severe nonlinearities in going from the concentration extremes on the curves, as measured by the changes in response factors (i.e., the ratio of the response units, area or peak height, to the mass of material injected). However, over the concentration spans from the lowest to the highest pairs in the interlaboratory study, only DMP and DEP have severe response factor changes, dropping from 1 at the lowest pair to the range of 0.15 to 0.25 at the highest pair. If the calibration curves prepared by the participants for these two compounds did not adequately reflect these large changes in response factors, major errors in accuracy could have resulted. Response factor changes are fairly minor for the other phthalates and should not have affected analytical accuracy materially.

As may be seen in Table 18, the lowest spiking levels used in the study were nearly equal to the MDL in some instances for DEP, BBP and 2EHP and only twice the MDL in some instances for DMP, DBP and DOP. In no case was the lowest spiking level more than seven times the MDL. Although these levels are thought to be lower than desirable, accuracy did not increase when the spiking levels increased. Therefore, the low ratios of spiking concentrations to MDLs that occurred in some instances with the lowest Youden pair appear to be of no consequences in this study.

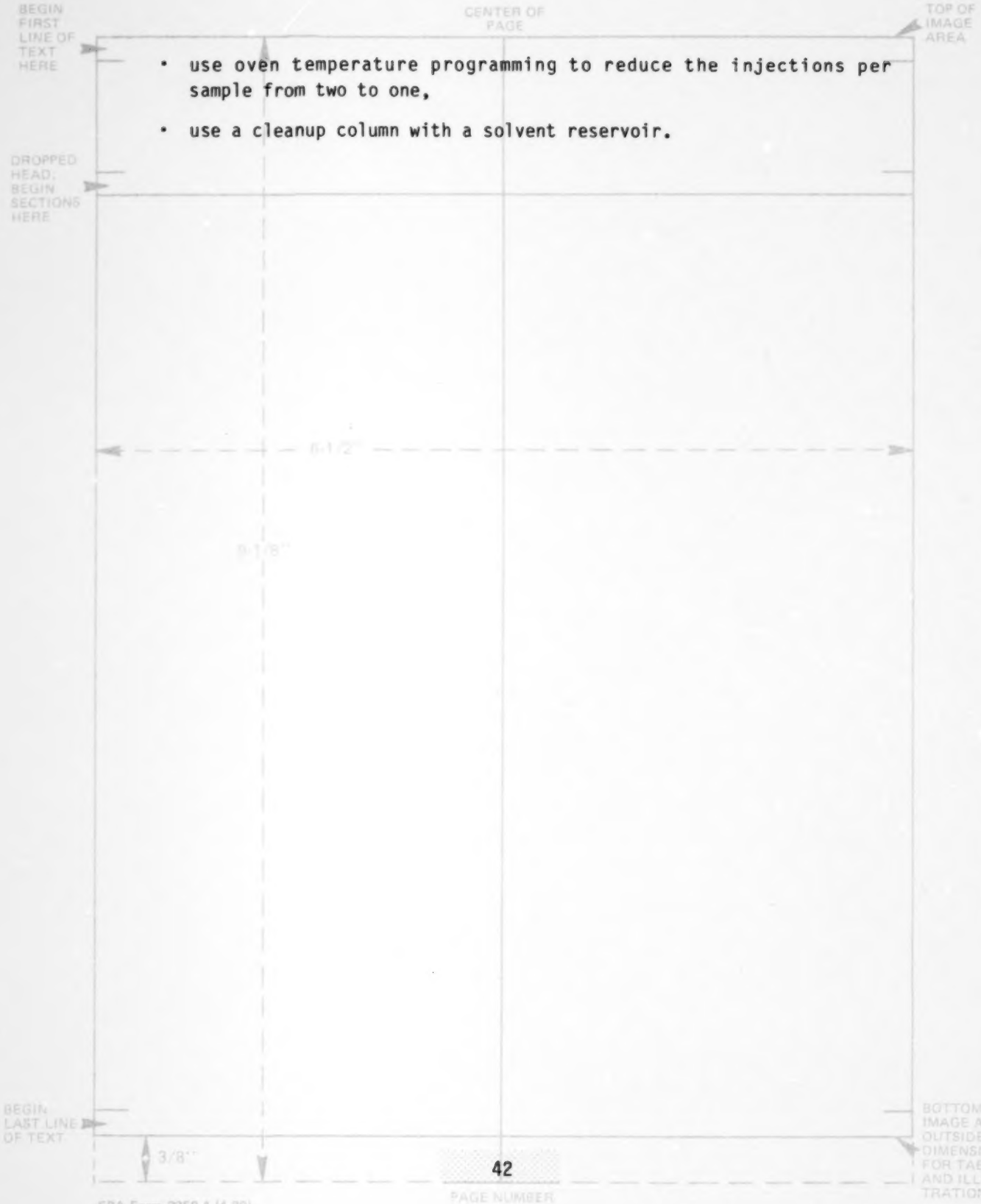
The principal problem reported by eight participants was inconsistent interferences which caused inconsistent recoveries to be obtained, with three laboratories noting this problem was especially bad with respect to DMP, DEP and 2EHP. One laboratory noted that interference in the BBP region of the chromatograms was the most troublesome.

Two participants blamed low bath temperatures during Kuderna-Danish concentrations for excessive time spent for analysis and as a possible cause of excess losses of analytes.

Three participants suggested that nonlinear responses, especially for DMP and DEP, caused less accurate results to be obtained.

Two participants claimed losses of phthalates occurred during the 40-mL elution with hexane after the sample had been put on the Florisil column.

Recommendations for method improvements, besides raising the bath temperatures for the concentration step, are as follows: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- use oven temperature programming to reduce the injections per sample from two to one,
- use a cleanup column with a solvent reservoir.

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REFERENCES

1. Code of Federal Regulations, 40:Part 136, October 16, 1973.

2. U.S. Code Congressional and Administrative News, 3, 1977, 95th Congress, First Session 1977.

3. Federal Register 44, 233, 69491-69495, December 3, 1979.

4. Youden, W. J. Statistical Techniques for Collaborative Tests. Association of Official Analytical Chemists, Washington, D.C., 1969.

5. Burke, J. A., J. Amer. Chem. Soc., 48:1037, 1965.

6. Outler, E. C. and McCreery, J. H. Interlaboratory Method Validation Study: Program Documentation. Battelle Columbus Laboratories, 1982.

7. Bishop, T. A., Brydon, F. E., and Outler, E. Development of Appropriate Statistical Techniques to Compare Analytical Methods Across Wastewaters. Battelle Report to Environmental Protection Agency.

8. Thompson, W. R. Annals of Mathematical Statistics, 6:214, 1935.

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TABLE A-1

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DIMETHYL PHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
TRUE VALUE UG/L	1.75	2.24	1.75	2.24	1.75	2.24	1.75	2.24	1.75	2.24	1.75	2.24
LABORATORY NUMBER												
601	0.70	1.70	1.00	0.90	0.40	1.90	1.90	2.30	0.30	0.80	0.70	1.90
602	< 2.50*<	2.50*<	2.50*<	2.50*	2.92 <	2.50*<	2.50*<	2.50*<	2.50*<	2.50*	8.92*<	2.50*
603	0.78	0.70	0.82	0.72	5.58*	5.34	1.10	1.99	0.96	1.48	0.00*	0.00*
604	16.80*	24.80*	6.00*	0.20	*	*	*	*	*	*	*	*
605	92.00*	32.60*	9.06*	31.10*	35.60*	45.00*	4.39*	*	4.18*	5.03*	*	3.45*
606	62.20*	66.80*	94.50*	77.70*	63.60*	69.60*	*	104.00*	97.70*	*	102.00*	72.90*
607	1.44	2.89	1.36	3.69	1.26	1.64	1.08	1.45	0.96	1.58	0.19	0.53
608	2.38	1.57	2.42	10.50*	1.98	2.38	1.31	1.26	1.56	0.97	1.47	1.23
609	1.52	3.31	1.46	1.61	2.28	2.76	1.11	3.34	0.69	1.84	1.37	2.07
610	3.35	4.74	0.92	3.64	*	3.64	4.54*	6.36*<	0.91*	8.18*	3.22	3.62
611	0.23	15.20*	1.48	1.15	1.48	1.78	1.43	1.05	5.08*	3.30	*	*
612	0.80	0.80	1.54	1.92	1.38	3.73	*	*	*	0.05*	3.63	0.13
613	1.32	2.02	0.78	1.72	1.11	2.61	2.51	2.56	1.47	2.60	1.10	2.24
614	0.50	0.78	0.44	0.83	0.45	0.73	0.42	0.77	0.44	0.57	0.47	0.67
615	1.33	2.80	2.50	3.00	2.00	2.00	1.68	3.00	*	0.20	4.02*	5.22*
616	1.04	1.67	2.54	1.59	1.13	0.25	1.20	1.43	1.75	1.27	1.51	1.67

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-1 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DIMETHYL PHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
TRUE VALUE UG/L	9.60	12.30	9.60	12.30	9.60	12.30	9.60	12.30	9.60	12.30	9.60	12.30
LABORATORY NUMBER												
601	4.90	9.90	6.70	4.40	4.90	4.70	3.70	6.70	7.00	9.00	9.50	7.10
602	6.43*	3.30*	4.55*	*	6.48	6.62	4.52	5.56	4.98	8.07	16.10	11.30
603	1.44	2.94	3.07	5.63	9.14	10.50	6.32	7.89	6.03	7.20	0.00*	4.90
604	24.80*	23.80*	11.20	24.20	*	*	*	*	*	*	*	*
605	133.00*	*	35.50*	34.50*	10.40*	6.16*	41.80*	1.89*	64.50*	5.26*	79.70*	13.10*
606	89.00*	84.10*	97.80*	98.70*	82.70*	84.70*	89.60*	108.00*	106.00*	97.00*	105.00*	113.00*
607	7.48	5.52	8.84	10.00	7.72	10.30	6.01	9.92	7.21	10.10	5.84	9.54
608	9.70	9.50	5.75	5.60	4.43	18.50	8.09	14.40	6.39	6.95	6.44	10.20
609	8.05	10.00	9.20	9.26	8.05	10.26	9.20	6.75	8.05	12.75	5.75	5.75
610	14.10	20.90	9.98	22.30	15.00*	19.10	12.70*	15.90*	6.82	16.90	7.32	15.90
611	4.42	9.79	6.62	3.52	6.08	7.36	4.79	2.81	5.25	6.79	*	3.00
612	3.73	7.38	9.57	13.10	6.46	5.15	*	*	*	0.33*	14.60	35.70*
613	8.21	9.52	7.57	2.05*	6.81	9.63	10.00	11.80	6.88	13.30	7.89	14.00
614	6.50	7.43	6.60	7.27	6.40	7.27	6.03	6.72	5.31	6.19	4.70	6.01
615	13.50	24.40	26.00*	27.30	8.50	21.70	14.00	31.60*	5.70	10.00	17.70*	27.30*
616	6.10	8.23	6.19	*	6.33	6.62	3.66	3.72	4.33	5.53	5.82	5.72

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE A-1 (CONT'D)

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
	2	6	2	6	2	6	2	6	2	6	2	6
MEAN STUDENT PAIR	21.00	26.93	21.00	25.98	21.06	25.90	21.00	26.96	21.00	26.96	21.00	26.93
TRUE VALUE UG/L												
LABORATORY NUMBER												
601	7.10	14.93	5.92	9.40	6.76	6.80	9.60	14.00	6.20	10.00	9.93	10.40
602	9.70*	6.27*	5.91*	6.93*	17.10	9.93	3.48	15.76 <	2.98*	11.40	2.89	14.56
603	8.87	13.62	13.70	15.83	11.70	16.76	13.30	20.30	14.00	19.70	3.03	16.10
604	67.03*	43.03*	74.25	43.80	*	*	*	*	*	*	*	*
605	6.14*	77.13*	*	55.23*	3.58*	11.90*	31.10*	37.90*	*	71.70*	23.93*	*
606	108.23*	102.63*	131.93*	129.03*	94.00*	99.00*	101.00*	103.00*	128.30*	126.00*	133.03*	98.20*
607	19.93	12.93	17.63	13.83	10.30	14.00	16.40	13.76	14.60	14.90	8.33	12.60
608	10.50	8.49	9.89	15.40	13.00	15.80	11.20	20.20	7.92	10.80	12.60	23.90
609	18.40	22.09	14.69	20.03	23.06	29.00	14.00	29.00	23.40	29.00	17.60	31.00
610	23.20	30.93	25.93	35.53	25.00	33.20	22.60*	42.30*	25.50	29.50	16.30	24.40
611	16.50	27.33	14.60	20.40	11.40	33.30	14.10	24.90	13.20	29.00	9.89	9.17
612	6.00	15.40	16.20	25.70	11.90	20.00	*	*	*	*	27.00	58.40*
613	14.03	28.30	9.20*	24.63	14.60	26.50	14.70	28.10	11.90	29.30	18.30	32.60
614	17.60	17.93	17.90	19.03	16.40	17.60	10.80	10.60	15.70	14.60	14.03	14.40
615	19.03	21.53	20.30	23.90	17.50	12.00	25.60	22.70	21.00	21.10	24.10*	26.50*
616	13.40	8.51	13.73	13.33	11.00	14.00	15.30	7.56	13.10	9.91	19.73	13.20

* = REJECTED

WATER LEGEND

1 = DISTILLED WATER
2 = TAP WATER
3 = SURFACE WATER
4 = WASTE WATER 1
5 = WASTE WATER 2
6 = WASTE WATER 3

TABLE A-2

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DIETHYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
TRUE VALUE UG/L	2.11	1.70	2.11	1.70	2.11	1.70	2.11	1.70	2.11	1.70	2.11	1.70
LABORATORY NUMBER												
601	0.90	1.40	1.40	1.10	0.60	1.90	2.30	2.10	0.50	1.20	1.60	1.90
602	2.02	1.56	3.31	1.72	4.61 <	1.50*<	1.50*<	1.50*	3.92*<	2.50*	6.21*<	4.37*
603	1.51	2.02	3.37	1.67	6.56	5.32*	3.84	4.29	8.25*	5.20*	*	*
604	0.98	9.70*	1.75	0.76	4.10	2.90	7.00	*	*	4.20	*	*
605	4.15*	3.70*	1.79*	16.80*	1.23*	15.00*	2.71*	*	*	3.41*	5.14*	0.79*
606	21.40*	7.40*	12.80*	21.00*	25.20*	30.60*	39.80*	47.10*	50.40*	48.40*	57.10*	38.10*
607	2.94	2.56	2.91	1.98	2.76	1.59	3.84	1.40	1.75	1.39	2.42	2.13
608	1.45	1.10	1.28	1.70	1.36	1.80	2.51	2.27	6.23*	1.51	2.66	2.06
609	0.15	0.13	0.29	0.10	0.14	0.12	0.09	0.17	0.09	0.15	0.13	0.16
610	3.53*	6.57*	8.18*	8.19*	*<	0.91*	4.27 <	4.54*<	0.91*<	9.09*	24.50*<	19.10*
611	1.07	2.45	2.49	1.12	1.69	1.05	2.22	0.45	1.49	3.30	*	*
612	22.20*	1.67	2.67	1.93	1.93	1.60	0.80	1.80	1.67	1.34	7.87*	3.91*
613	2.07	1.77	1.95	1.41	1.72	1.90	1.61	1.66	1.61	1.41	2.48	2.17
614	0.68	0.87	0.62	0.84	0.68	0.80	0.59	0.70	0.61	0.77	0.57	0.70
615	2.00	1.20	3.00	1.50	2.00	0.36	2.70	2.00	0.97	0.58	0.69	1.14
616	0.92	0.63	2.52	0.70	0.86	0.16	0.52	0.48	0.40	0.29	0.86	0.52

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-2 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

****EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DIETHYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
TRUE VALUE UG/L	12.60	10.20	12.60	10.20	12.60	10.20	12.60	10.20	12.60	10.20	12.60	10.20
LABORATORY NUMBER												
601	7.70	8.40	8.60	7.00	7.70	4.60	3.80	4.80	7.80	8.70	12.40	5.00
602	7.92	3.56	5.29	*	9.34	8.28	7.26	6.21	10.20	8.94	27.00	5.63
603	5.19	6.75	9.59	6.95	10.40	9.40	15.40	11.00	26.70*	17.70*	3.92	4.32
604	7.60	4.30	10.50	7.60	*	9.60	31.50*	32.00	17.80	12.60	*	*
605	42.50*	*	98.00*	12.60*	55.80*	51.80*	94.00*	13.80*	98.30*	65.00*	36.70*	0.66*
606	24.20*	20.10	19.40*	21.70*	18.90*	25.30*	28.20*	46.00*	49.40*	47.60*	49.50*	40.70*
607	8.19	4.68	10.60	8.55	10.10	9.58	7.34	8.74	9.70	9.20	9.76	17.20
608	10.60	9.59	9.72	9.97	8.37	7.34	15.90	25.70	14.20	5.20	16.70	10.60
609	1.08	8.54	1.08	9.50	1.51	9.50	1.18	9.03	1.08	10.93	1.18	10.45
610	15.00*	16.80*	20.00*	19.10*	23.80*	19.50	16.90	14.60	12.70	16.20	24.50	28.20
611	8.06	8.13	17.40	6.93	11.10	5.00	10.20	6.00	10.10	6.93	2.78	5.20
612	12.40	10.70	14.70	12.90	11.10	5.07	8.89	6.13	8.37	10.97	25.47*	35.47*
613	13.00	10.00	13.70	3.76*	10.40	8.97	9.55	10.10	11.10	10.60	12.30	11.30
614	8.18	7.95	8.40	7.83	8.52	7.96	8.64	7.70	8.06	7.43	8.15	7.17
615	11.20	20.00	19.00	13.20	12.00	18.00	10.50	26.00	7.90	6.56	8.67	20.40
616	2.87	2.48	2.67	*	2.87	2.29	2.90	0.67	1.89	1.15	1.95	1.61

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-2 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DIETHYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	6	2	5	2	6	2	6	2	6	2	6
TRUE VALUE UG/L	27.40	22.20	27.40	22.20	27.40	22.20	27.40	22.20	27.40	22.20	27.40	22.20
LABORATORY NUMBER												
601	7.80	14.10	4.90	10.00	5.80	8.00	16.40	12.90	7.00	19.50	14.00	10.80
602	8.60	5.07	5.39	11.90	23.50	12.70	4.56	14.30	7.38	12.10	4.09	12.10
603	20.80	18.70	23.20	20.10	29.40	21.10	29.50	23.10	37.10*	30.50*	27.20	5.20
604	31.00	19.50	19.00	15.50	24.00	23.00	35.50	36.00	93.80*	34.00	*	*
605	15.90*	*	39.60*	57.00*	12.60*	60.60*	15.90*	82.80*	8.72*	73.20*	*	41.00*
606	22.60	22.80	19.60*	24.20*	23.20*	21.90*	44.10*	49.10*	48.20*	46.80*	58.30*	45.70*
607	14.00	12.10	14.90	9.54	16.00	12.20	15.10	12.50	26.70	17.00	47.80	23.20
608	13.30	10.30	13.00	15.20	17.30	14.20	18.70	20.40	11.40	13.50	15.60	23.80
609	21.46	14.76	14.29	16.16	26.64	15.68	38.51	17.10	29.23	19.06	30.34	20.90
610	33.20*	26.90*	38.20*	36.40*	40.00	29.10	36.80	29.60	40.90	25.10	41.10	35.30
611	23.00	20.80	22.50	19.90	19.00	21.80	23.00	16.70	19.00	18.70	19.50	13.00
612	22.20	21.60	26.70	24.00	19.30	18.40	1.67	16.00	33.27	22.67	47.47*	43.47*
613	21.90	22.80	4.65*	21.70	26.00	22.90	24.70	18.70	22.30	21.10	29.50	24.50
614	23.50	17.20	23.20	13.70	22.40	16.50	22.40	14.70	21.20	14.40	19.60	13.70
615	24.00	9.80	26.00	9.70	27.00	9.70	36.00	11.00	12.40	6.97	20.40	9.57
616	4.87	4.10	4.78	4.01	5.78	4.68	6.02	3.15	5.86	2.48	5.33	4.36

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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49
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TABLE A-3

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DI-N-BUTYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
TRUE VALUE UG/L	3.49	2.48	3.49	2.48	3.49	2.48	3.49	2.48	3.49	2.48	3.49	2.48
LABORATORY NUMBER												
601	1.80	2.50	2.60	1.40	2.30	1.30	3.20	2.00	0.60	1.00	2.10	1.30
602	2.93	1.14	3.72	1.58	2.59 <	0.70*	1.27 <	0.70*	2.23 <	1.94*	3.55 <	6.91*
603	2.87	2.19	4.37	2.31	2.74	2.05	2.06	1.16	4.85	1.66	8.59*	1.38
604	4.39	6.49*	9.09*	3.67*	4.89	3.89	6.43*	4.37*	0.45	3.38	*	3.85
605	13.30*	1.71*	1.06*	5.52*	0.04*	4.09*	5.30*	3.68*	8.72*	9.29*	0.15*	1.61*
606	2.58	2.58	3.57	2.40	5.54	3.29	4.99	4.29	3.20	3.05	5.00	2.98
607	2.49	3.64	1.20	3.45	1.70	1.37	1.75	0.64	1.53	0.88	1.84	1.65
608	3.59	0.93	0.93	4.65*	1.67	4.31	2.96	4.16	2.95	1.82	2.90	3.65
609	5.72*	3.57*	4.29	2.86	4.29	2.86	2.86	2.86	2.86	3.57	4.72*	3.57*
610	2.46	1.89	1.27	1.37	*	1.36	2.64	1.73 <	0.91*	0.54	2.18	0.82
611	1.91	2.55	2.64	1.91	2.19	1.78	2.28	2.48	2.64	1.91	1.00	1.03
612	2.97	1.75	3.39	2.33	2.67	2.06	1.88	2.06	3.11	2.56	3.07	2.07
613	3.41	3.19	3.82	2.64	3.32	2.90	2.95	2.11	3.20	2.59	3.13	2.56
614	1.41	1.19	1.56	1.33	1.56	1.19	1.61	1.26	1.56	1.26	1.36	0.98
615	3.46	2.21	5.08	2.57	3.79	3.45	3.48	2.66	6.59	3.09	3.47	2.52
616	2.13	2.81	12.90*	1.98	2.77	1.93	3.96	2.21	7.89	1.71	2.65	1.98

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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TABLE A-3 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DI-N-BUTYLPHTHALATE ANALYSTS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
TRUE VALUE UG/L	14.00	9.90	14.00	9.90	14.00	9.90	14.00	9.90	14.00	9.90	14.00	9.90
LABORATORY NUMBER												
601	5.90	7.90	9.60	6.00	5.70	4.00	3.80	5.50	7.80	7.50	12.40	4.50
602	12.60	5.72	12.00	*	20.40	6.45	5.03	5.21	30.60*	8.92	9.02	3.81
603	7.52	7.07	9.65	7.99	7.46	5.45	9.56	6.55	15.60	11.40	14.50	18.10
604	14.00	8.09	17.40*	11.90*	*	10.70	17.90*	17.20*	12.50	10.20	15.30	7.05
605	10.70*	*	7.64*	4.59*	9.95*	5.99*	31.60*	3.74*	13.80*	3.89*	8.89*	*
606	12.60	9.16	8.84	9.97	7.60	5.99	7.32	7.78	9.75	6.55	9.95	9.27
607	10.10	7.95	7.48	9.03	10.20	9.78	5.03	9.18	8.88	8.78	7.22	7.29
608	12.00	5.07	12.99	5.01	6.26	6.39	18.50	8.57	16.30	1.16	6.54	4.94
609	28.60*	14.29*	28.60*	11.90	22.88	11.90	21.45	10.71	21.45	14.28	21.45*	14.28*
610	9.99	9.13	10.20	8.96	12.10	9.45	11.70	7.91	3.18	4.63	9.33	7.83
611	9.65	8.60	12.30	7.60	12.80	7.60	12.50	8.41	16.90	7.80	4.73	7.60
612	11.95	9.25	12.90	10.00	10.70	3.80	11.30	7.00	11.30	9.33	11.37	8.36
613	13.20	9.84	16.25	7.15*	12.70	8.78	11.00	7.52	12.20	10.20	14.60	9.69
614	11.10	10.30	10.60	9.74	11.60	9.09	12.70	8.52	12.70	9.74	10.60	8.52
615	14.00	35.40*	22.10*	22.50*	15.10	22.30*	12.00	28.30*	14.80	11.20	13.40	20.70
616	10.70	10.20	9.22	*	6.12	5.55	14.50	5.59	14.80	9.60	14.40	8.78

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE A-3 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DI-N-BUTYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
TRUE VALUE UG/L	34.90	24.80	34.90	24.80	34.90	24.80	34.90	24.80	34.90	24.80	34.90	24.80
LABORATORY NUMBER												
601	6.40	18.50	8.90	12.80	8.30	33.20	9.00	18.80	5.40	16.90	8.00	12.00
602	31.00	10.10	21.40	12.50	27.30	15.20	7.19	23.60	16.20	18.30	7.83	14.00
603	53.30	35.00	51.70*	28.30	32.80	27.00	29.20	22.50	40.00	33.40	35.00	20.40
604	36.70	20.33	37.00*	25.60*	31.40	22.60	34.60*	28.60*	34.00	23.60	29.60	64.80*
605	3.80*	10.40*	4.92*	6.90*	9.61*	5.08*	35.80*	35.60*	9.52*	10.50*	8.88*	11.70*
606	15.50	10.60	17.00	15.90	16.70	16.40	12.20	9.68	16.30	11.60	15.10	13.40
607	24.10	22.80	22.10	18.80	22.30	23.40	19.30	23.10	30.20	18.10	21.40	20.40
608	14.80	20.00	33.70	9.47	32.80	19.70	28.10	14.80	30.40	13.70	28.40	21.80
609	29.49*	23.35*	25.65	25.01	39.05	21.68	29.49	25.01	32.05	25.01	32.05*	25.31*
610	28.03	23.53	29.00	20.00	29.80	21.20	26.70	19.20	22.20	16.80	24.00	16.60
611	27.60	30.90	26.40	29.20	28.80	30.00	32.70	24.50	29.60	28.30	28.40	28.30
612	28.15	21.75	30.00	23.30	22.80	17.50	27.20	22.30	33.30	24.50	28.87	24.47
613	26.20	23.70	6.94*	26.20	31.90	26.80	25.00	20.10	30.50	21.90	34.80	23.70
614	23.00	22.00	22.00	19.80	25.00	20.90	24.00	17.60	29.30	17.60	29.00	19.80
615	20.20	10.90	20.80	10.50	22.10	11.20	25.90	10.80	28.80	11.10	29.80	10.40
616	26.90	22.00	27.40	21.10	26.40	15.50	47.10	23.80	22.70	28.30	28.20	26.30

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-4

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR BUTYLBENZYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
TRUE VALUE UG/L	0.70	0.87	0.70	0.87	0.70	0.87	0.70	0.87	0.70	0.87	0.70	0.87
LABORATORY NUMBER												
601	0.70	0.30	0.70	0.20	1.40	2.50*	2.00*	0.40	0.20	0.10	0.70	1.10
602	0.89	0.55	0.84	0.80	0.72	1.55	0.32 <	0.20*	0.81 <	0.75*	0.45 <	0.82*
603	0.67	1.09	0.52	0.88	1.35	1.61	*	*	*	*	*	*
604	0.53	1.21	2.82*	0.61	0.43	0.70	0.80	0.35	0.90	0.86	0.48	0.58
605	5.07*	4.26*	5.04*	5.98*	2.84*	8.78*	9.81*	5.98*	3.47*	10.00*	3.68*	13.70*
606	0.96	1.22	1.28	0.81	1.06	1.41	0.84	0.40	1.22	1.27	1.02	0.82
607	0.86	1.38	0.98	1.23	0.88	1.18	0.51	0.31	1.27	1.36	0.69	0.42
608	0.35*	0.15*	0.21	0.39	0.26	0.72	0.44	0.66	0.55	3.74*	0.60	1.05
609	0.62	1.08	0.59	0.77	0.59	1.08	0.71	1.12	0.77	0.77	0.80	0.54
610	8.18*	5.00*<	1.00*	3.45*	*<	1.00*	5.64*<	3.54*<	1.00*<	20.50*	29.50*<	1.00*
611	0.21	0.41	0.57	0.87	0.43	1.48	0.50	0.92	0.40	0.82	0.14	0.51
612	0.46	0.61	0.74	0.89	0.71	0.96	0.43	0.83	0.69	0.97	0.59	0.86
613	0.80	1.22	0.71	1.09	0.65	1.06	0.52	1.04	0.52	0.88	0.70	0.87
614	0.87	1.06	0.89	1.28	0.76	1.25	0.84	1.00	0.87	1.15	0.76	1.13
615	0.73	0.59	0.81	0.85	0.76	0.72	1.21	1.00	0.19	0.67	1.05	1.31
616	16.90*	5.81*	22.20*	4.33*	24.70*	4.23*	22.60*	6.41*	13.05*	6.17*	6.54*	7.83*

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TYPING GUIDE SHEET
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 327)
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53
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TABLE A-4 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR BUTYLBENZYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
TRUE VALUE UG/L	4.18	5.23	4.18	5.23	4.18	5.23	4.18	5.23	4.18	5.23	4.18	5.23
LABORATORY NUMBER												
601	3.00	5.70	5.40	5.80	4.80	4.30	1.30	4.50	3.20	5.10	3.40	3.00
602	4.53	2.91	4.17	*	4.32	3.87	1.76	3.14	3.95	3.32	2.97	4.21
603	3.37	4.74	3.16	4.49	4.52	5.96	0.33*	2.19*	3.50	4.34	*	10.50
604	3.29	3.74	3.42	3.89	*	3.32	3.16	3.56	3.06	4.35	2.07	2.27
605	16.00*	14.50*	16.20*	15.90*	21.00*	29.80*	17.30*	16.90*	23.10*	15.50*	27.00*	36.60*
606	3.93	3.13	2.97	5.00	4.04	4.80	3.84	4.12	3.03	3.90	3.14	4.08
607	3.52	5.82	3.48	7.12	3.91	5.88	0.91	6.27	4.04	7.49	1.72	6.54
608	3.06*	3.27*	2.42	4.33	1.35*	4.82	4.38	5.17	3.52	0.79	3.27	5.17
609	4.24	2.10	4.62	2.63	3.47	3.20	4.43	3.53	3.66	4.05	3.85	4.35
610	9.54*	26.80*	9.54*	17.30*	14.50*	14.50	7.73	45.00*	37.20*	18.20*	10.00*	18.60*
611	3.08	5.31	3.45	10.40	4.74	7.97	4.22	5.75	4.92	6.20	3.39	7.08
612	2.96	4.00	4.35	5.74	3.68	2.88	3.92	4.35	3.84	5.56	4.00	4.70
613	4.03	4.67	3.54	1.71*	3.53	4.73	2.59	3.74	3.53	4.00	2.45	4.29
614	4.04	5.43	4.64	5.35	4.00	5.27	4.00	4.94	4.16	5.59	3.92	4.78
615	4.00	12.00*	5.05	12.00	4.78	12.00	3.91	12.00*	3.61	4.65	4.44	10.70
616	11.90*	7.70*	22.40*	*	277.00*	12.10*	137.00*	11.80*	12.40*	8.84*	7.90*	33.10*

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-4 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR BUTYLBENZYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	6	2	6	2	6	2	6	2	6	2	6
TRUE VALUE UG/L	9.75	12.20	9.75	12.20	9.75	12.20	9.75	12.20	9.75	12.20	9.75	12.20
LABORATORY NUMBER												
601	4.40	11.10	2.50	8.10	2.50	10.60	5.90	8.40	3.60	10.70	5.00	9.00
602	7.81	6.29	7.72	7.45	10.30	10.00	2.31	6.16	8.54	11.10	7.30	10.40
603	8.97	9.54	7.98	10.10	8.90	10.60	4.94*	6.91*	8.20	9.90	17.90*	52.50*
604	6.72	7.48	6.53	6.82	60.04*	7.39	6.82	7.97	7.26	8.52	5.54	6.92
605	15.80*	29.80*	19.10*	37.40*	22.40*	26.10*	41.60*	45.00*	13.30*	45.80*	33.30*	51.60*
606	6.84	9.60	4.56	8.88	8.52	10.20	6.16	4.84	7.96	9.80	8.40	5.96
607	9.27	14.10	9.91	11.56	8.42	6.02	7.17	11.80	13.00	11.80	7.79	11.30
608	3.29*	5.01*	4.31	3.24	7.40	9.97	6.72	8.06	4.76	9.22	6.29	9.39
609	12.58	13.51	11.84	14.25	12.86	14.43	12.30	14.43	8.42	14.52	7.77	13.32
610	46.80*	24.50*	42.70*	32.30*	26.80*	29.50*	42.70*	48.20*	45.00*	26.80*	55.00*	64.50*
611	5.14	13.80	6.69	14.53	6.32	13.80	5.93	13.60	6.32	14.00	5.84	11.80
612	6.00	8.34	9.18	12.23	7.18	9.27	8.36	11.80	10.40	13.40	8.91	11.70
613	7.27	11.10	1.56*	10.40	8.91	12.20	5.86	7.58	6.85	9.08	6.44	10.00
614	10.90	13.40	11.20	13.60	10.90	10.40	10.60	12.40	10.30	11.50	10.90	10.20
615	8.92	5.50	9.94	5.91	10.60	5.29	9.61	5.38	9.90	5.36	8.17	7.25
616	18.80*	20.50*	16.10	24.20*	21.30*	25.10*	28.10*	35.50*	54.90*	32.30*	52.50*	25.20*

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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TABLE A-5

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR BIS-2-ETHYLHEXYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
TRUE VALUE UG/L	5.07	6.95	5.07	6.95	5.07	6.95	5.07	6.95	5.07	6.95	5.07	6.95
LABORATORY NUMBER												
601	22.00*	85.20*	21.50*	25.60	24.00	64.90*	53.10*	12.80	18.00*	10.60	27.00	52.10
602	8.26	6.98	2.80	5.84	2.30	24.50	1.97 <	0.90*	5.21 <	5.62*	3.35 <	6.49*
603	*	*	0.37	1.50	*	*	3.05	2.90	1.59	*	*	1.09
604	0.74	1.25	3.85	4.42	6.22	4.84	4.33	167.00*	5.48	4.85	8.10	1.48
605	2.55*	10.20*	0.43*	13.00*	16.00*	17.80*	12.00*	7.26*	4.04*	21.10*	18.00*	33.80*
606	6.15	*	5.28	3.30	5.72	5.04	3.40	4.96	5.44	5.40	5.28	5.40
607	5.96	49.30*	*	28.60	10.00	42.40*	*	16.50	83.30*	40.60	10.80	41.10
608	1.36	0.63	1.77	3.19	2.60	7.29	1.34	4.52	3.47	40.60	3.33	4.99
609	3.30	9.60	4.50	8.64	5.11	12.96	4.80	7.68	4.80	11.52	4.20	10.08
610	37.70*	8.64	3.18	11.40	*	5.00	26.90	12.70	4.54	22.90	47.30	10.50
611	3.56	4.24	6.04	7.84	3.25	9.57	5.58	0.78	4.42	12.40	*	3.45
612	0.96	1.52	3.44	5.64	19.67	4.37	1.11	2.72	1.07	4.13	31.24	8.54
613	311.00*	30.00*	267.00*	469.00*	46.90*	36.40*	449.00*	465.00*	220.00*	131.00*	173.00*	36.70
614	5.56	8.41	6.92	9.50	6.50	7.62	5.87	6.53	5.97	6.39	*	6.22
615	*	*	84.80*	10.70	*	24.00	32.60	0.39	2.23	6.90	*	*
616	9.40	13.70	9.69	1.42	26.10	1.19	0.93	1.58	3.55	2.22	2.08	2.21

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-5 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR BIS-2-ETHYLHEXYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
MEDIUM YOUDEN PAIR	4	5	4	5	4	5	4	5	4	5	4	5
TRUE VALUE UG/L	20.30	27.80	20.30	27.80	20.30	27.80	20.30	27.80	20.30	27.80	20.30	27.80
LABORATORY NUMBER												
601	10.50	33.80	197.00*	96.30	159.00*	40.60	29.20	57.90	23.20	28.30	22.80	57.90*
602	27.70	20.20	12.00	*	23.10	13.70	6.81	17.30	21.40	10.20	14.90	24.60
603	*	3.80	12.10	16.90	9.41	20.10	12.50	86.40*	4.65	10.70	6.02	11.40
604	3.61	9.67	17.60	25.90	*	11.60	16.50	32.50	17.30	25.30	5.82	11.00
605	5.76*	8.05*	10.90*	12.40*	19.30*	31.90*	15.60*	32.40*	15.20*	11.40*	15.60*	16.50*
606	7.92	7.54	9.76	7.15	13.00	8.80	13.10	8.20	8.80	11.70	8.96	11.60
607	54.90*	9.60	55.40*	16.20	76.20*	33.50	42.50	8.20	90.00*	27.70	62.30	20.50
608	5.11	4.83	15.50	36.70	7.24	39.80	20.50	35.70	18.40	3.55	8.55	21.20
609	15.60	32.76	15.80	22.30	12.00	23.66	17.04	32.31	15.60	32.76	16.80	36.40
610	10.90	10.00	22.80	26.90	33.20	32.70	25.50	39.50	40.50	34.10	*	35.50
611	3.06	26.60	3.34	40.10	4.45	33.10	5.34	30.10	4.32	25.40	3.42	28.90
612	3.87	4.67	13.52	25.52	14.87	13.17	10.78	16.28	15.85	23.75	26.44	26.84
613	23.00	22.70	220.00*	62.30*	51.10*	57.80*	655.00*	363.00*	145.00*	286.00*	40.90	30.30
614	19.00	22.30	22.80	22.50	25.00	*	19.20	22.10	21.50	26.20	24.10	19.60
615	*	0.80*	12.50	24.80	*	*	13.00	36.50	46.80	17.30	46.50	408.00*
616	5.67	8.55	5.74	*	4.75	8.43	5.28	8.34	4.82	9.10	8.31	7.78

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TYPING GUIDE SHEET

TABLE A-5 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR BIS-2-ETHYLHEXYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
HIGH YOUDEN PAIR	2	6	2	5	2	6	2	6	2	6	2	6
TRUE VALUE UG/L	40.60	55.60	40.60	55.60	40.60	55.60	40.60	55.60	40.60	55.60	40.60	55.60
LABORATORY NUMBER												
601	73.50	23.50	49.30	26.20	21.50	29.40	61.40	24.40	70.30	32.70	24.00	29.00
602	39.60	29.70	25.70	3.38	44.80	25.40	8.49	18.80	31.80	50.70	31.00	43.80
603	36.60	4.39	30.40	36.40	38.10	32.60	43.80	40.80	29.40	33.30	35.80	30.40
604	15.00	76.40	33.90	47.70	18.40	41.30	54.90	46.20	37.40	48.90	26.80	72.60
605	5.37*	11.40*	12.40*	35.30*	19.00*	21.80*	31.00*	129.00*	7.92*	25.70*	22.10*	30.40*
606	11.50	15.10	10.50	11.10	10.80	14.80	11.00	12.20	17.80	25.20	20.40	29.60
607	6.52	24.10	16.50	37.90	23.90	24.10	*	659.00*	38.50	49.60	20.40	38.20
608	9.94	38.30	26.80	19.40	44.10	49.30	25.30	38.50	10.70	42.90	16.60	33.80
609	38.00	26.00	46.00	62.50	30.00	62.00	57.00	66.50	45.00	66.50	43.00	60.00
610	37.70	6.82	40.50	59.10	40.90	50.50	51.20	63.20	42.80	38.70	55.00	68.60
611	1.88	44.20	26.40	41.80	23.80	37.60	26.30	38.50	2.51	19.60	27.90	17.20
612	*	5.47	34.67	44.42	26.67	40.97	24.18	35.88	63.05	46.35	27.34	43.34
613	32.10	50.70	135.00*	240.00*	65.10*	106.00*	549.00*	357.00*	225.00*	330.00*	46.20	51.80
614	41.10	61.00	44.30	57.70	40.10	56.50	41.40	*	40.10	65.90	46.90	63.80
615	8.40*	*	17.20	57.00	*	*	21.70	16.50	85.00	30.10	38.60	24.90
616	13.10	15.10	13.80	15.40	13.30	14.60	12.50	15.20	13.70	16.90	18.70	20.80

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-6

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

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***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DI-N-OCTYLPHTHALATE ANALYSIS BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	3	1	3	1	3	1	3	1	3	1	3	1
TRUE VALUE UG/L	17.70	14.10	17.70	14.10	17.70	14.10	17.70	14.10	17.70	14.10	17.70	14.10
LABORATORY NUMBER												
601	4.20	4.30	8.40	3.40	3.80	29.30*	10.10	2.10	2.10	1.60	5.50	14.50
602	15.60	4.60	12.10	7.60	5.91	9.60	6.01 <	1.20*	17.10 <	9.47*	12.20 <	14.70*
603	7.89	6.60	14.60	13.20	15.70	14.00	11.10	10.40	7.22	10.70	9.51	8.11
604	1.03	1.67	20.00	13.10	6.49	5.23	12.40	22.20*	15.90	9.44	14.10	1.50
605	9.04*	6.38*	13.10*	13.30*	12.30*	13.60*	29.70*	9.87*	8.04*	26.30*	6.73*	12.40*
606	7.20	*	8.04	7.06	9.13	7.96	7.84	*	8.34	5.40	6.81	5.80
607	0.24	0.07	10.00	16.40	5.34	10.90	202.00*	8.10	4.34	4.60	1.04	8.92
608	1.86	0.82	5.45	5.69	7.52	10.70	5.17	7.39	7.52	6.44	11.40	9.65
609	21.12*	8.00*	34.32	8.00	36.96*	11.00*	26.40*	12.00*	18.48*	12.30*	18.48*	8.00*
610	5.45	5.91	11.40	25.00	*	3.64	14.10	13.20 <	1.80*	9.60	92.60*	11.40
611	11.50	7.69	13.20	13.00	12.30	11.00	10.20	9.13	11.20	11.00	9.34	8.65
612	1.56	2.23	13.00	9.60	12.60	11.10	6.75	7.62	10.92	9.22	6.38	7.50
613	6.57 <	4.79*	12.30	10.80	12.20	12.00 <	2.93*<	6.84*<	4.89*	4.89	3.29 <	8.21*
614	20.80*	14.60*	20.80	15.90	19.00	15.30	20.20	13.70	18.20	13.10	21.70*	13.00*
615	4.80	6.57	11.40	4.80	13.10	12.20	10.20	6.46	6.42	6.87	4.86	2.92
616	4.23	6.15	16.20	4.35	10.10	6.58	12.00	9.16	17.90	7.72	7.06	4.17

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
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4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-6 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

SPIKED WATER VALIDATION STUDY - SPE METHOD 610

RAW DATA FOR DI-N-OCTYLPHTHALATE ANALYSIS OF WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
SPIKING POINTS PER	4	4	4	5	4	5	4	5	4	5	4	5
TRUE VALUE UG/L	20.70	50.30	20.70	50.30	20.70	50.30	20.70	50.30	20.70	50.30	20.70	50.30
LABORATORY NUMBER												
601	15.60	17.30	170.00	20.00	14.00	10.50	27.60	10.90	23.20	29.30	29.20	20.60
602	30.70	23.10	48.00	*	34.70	21.30	25.30	37.90	34.90	32.70	9.04	47.80
603	31.10	32.40	99.00	33.20	61.80	37.60	48.80	43.70	46.60	47.10	43.10	40.90
604	18.00	25.60	69.10	49.70	*	24.60	19.80	42.40	33.00	50.90	53.70	30.20
605	14.20*	12.90*	38.60*	30.10*	47.20*	47.30*	40.90*	27.10*	44.90*	31.20*	33.90*	25.20*
606	19.30	22.60	19.30	22.00	18.40	14.30	10.40	14.70	20.00	18.00	22.00	19.00
607	37.80	17.00	95.00	38.00	80.60	64.50	60.10	52.60	75.10	33.30	77.40	30.40
609	18.30	9.10	98.20	39.40	21.60	93.50	70.60	44.10	62.60	9.53	52.00	37.60
609	90.00*	46.30*	170.00	42.00	90.30*	34.00*	90.00*	64.00*	102.30*	32.00*	86.00*	72.30*
610	8.92	7.27	78.10	37.30	67.70	33.70	64.10	48.60	51.40	31.40	*	37.30
611	42.80	48.40	47.30	47.20	60.50	50.70	63.00	48.10	63.20	49.60	49.20	48.40
612	9.50	4.10	98.80	48.40	35.30	30.60	38.80	32.60	30.72	44.32	34.10	29.40
613	3.30*	3.36	48.40	13.60*	33.10	44.10	16.60*	15.60*	29.80	20.50	20.90	18.70
614	33.30*	40.70*	51.80	42.00	61.10	48.50	54.90	42.20	53.30	47.90	38.90*	43.30*
615	5.90	10.80	32.60	47.70	50.70	63.70	47.40	75.70	38.70	12.00	48.90	85.10*
616	29.10	24.30	60.90	*	25.60	23.40	31.10	30.50	24.60	28.80	70.50	25.70

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE A-6 (CONT'D)

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

***EPA METHOD VALIDATION STUDY - SRI PHTHALATE EST

RAW DATA FOR DI-N-OCTYLPHTHALATE ANALYSIS BY WATER TYPE

HIGH TOUDEN PAIR	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
	2	6	2	6	2	6	2	6	2	6	2	6
TRUE VALUE UG/L	106.00	84.50	106.00	84.50	106.00	84.50	106.00	84.50	106.00	84.50	106.00	84.50
LABORATORY NUMBER												
601	62.00	44.40	9.30	23.20	19.90	37.30	35.50	30.90	22.90	38.90	30.30	33.20
602	74.20	35.90	99.60	33.00	94.50	29.10	19.10	29.30	87.20	71.30	77.00	64.30
603	68.40	35.50	100.00	76.90	100.00	79.40	79.80	66.10	79.80	59.90	70.30	51.30
604	32.70	48.40	93.10	75.00	53.70	41.90	86.40	68.20	96.00	72.10	80.80	54.60
605	14.70*	18.90*	30.70*	42.50*	37.70*	25.20*	69.40*	49.20*	20.40*	47.20*	47.70*	47.60*
606	27.00	30.60	21.90	31.20	24.70	39.50	19.10	24.60	18.80	35.00	22.00	24.40
607	24.00	38.00	98.40	91.90	86.50	35.90	84.50	5.90	101.00	62.40	82.00	67.40
608	17.40	28.70	47.00	15.80	81.40	65.30	59.40	25.80	41.60	39.40	86.30	40.00
609	256.00*	128.00*	148.00	136.00	272.00*	132.00*	232.00*	124.00*	196.00*	128.30*	152.00*	124.00*
610	35.00	6.36	90.00	73.60	89.10	66.40	105.00	65.00	86.80	60.50	95.40	62.30
611	51.30	65.20	65.80	58.80	84.00	52.20	79.30	53.70	65.33	51.20	85.70	87.00
612	27.10	5.44	85.30	62.50	75.00	61.20	58.80	52.90	90.32	63.42	52.90	50.60
613	9.78	8.98	13.70*	84.00	83.90	76.80	31.30*	22.50*	46.00	31.30	42.40	35.80
614	114.00*	89.90*	114.00	99.90	113.00	76.50	99.30	84.50	92.80	78.70	108.00*	72.10*
615	18.60	7.89	46.90	29.90	84.50	42.30	76.00	21.10	77.40	45.00	47.50	39.30
616	41.10	25.60	99.90	42.90	43.10	35.80	81.90	40.20	49.40	45.90	64.20	47.30

* = REJECTED

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

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APPENDIX B
EPA METHOD 606 (PHTHALATE ESTERS)

PHTHALATE ESTERS

METHOD 606

1. Scope and Application

1.1 This method covers the determination of certain phthalate esters. The following parameters may be determined by this method:

Parameter	STORET No.
Benzyl butyl phthalate	34292
Bis(2-ethylhexyl) phthalate	39100
Di-n-butyl phthalate	34110
Di-n-octyl phthalate	34596
Diethyl phthalate	34336
Dimethyl phthalate	34341

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in

Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary

considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of the analysis. Of particular importance is the avoidance of plastics because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4. Apparatus and Materials

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle - amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps - Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is

not corrosive.

4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel - 2000 ml, with Teflon stopcock.

4.3 Drying column - 20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column - two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture or flame ionization detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column - 300 mm long x 10 mm ID with coarse fritted disc at bottom and Teflon stopcock (Kontes K-420540-0213 or equivalent).

5. Reagents

5.1 Preservatives:

5.1.1 Sodium hydroxide - (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride - Pesticide quality or equivalent.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric

flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Diethyl Ether - Nanograde, redistilled in glass if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.6 Florisil - PR grade (60/100 mesh); purchase activated at 1250°F and store in dark in glass container with ground glass stoppers or foil-lined screw caps.

5.7 Alumina - Activity Super I, Neutral, W200 series, (ICN Life Sciences Group, No. 404583).

5.8 Hexane - Pesticide quality.

6. Calibration

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will

completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 ug/l in the final extract, for example, prepare standards at 10 ug/l, 50 ug/l, 100 ug/l, 500 ug/l, etc. so that injections of 1-5 ul of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. Quality Control

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

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7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and

completely analyzed within 30 days of collection.

9. Sample Extraction

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample pH with wide-range paper and adjust to within the range of 5-9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

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9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20-30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 Increase the temperature of the hot water bath to about 80°C. Momentarily remove the Snyder column, add 50 ml of hexane and a new boiling chip and reattach the Snyder column. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent

extract as before. Elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 ml of hexane, and adjust the volume to 10 ml. A 5-ml syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. Cleanup and Separation

10.1 If the entire extract is to be cleaned up by one of the following two procedures, it must be concentrated to about 2 ml. To the concentrator tube in 9.6, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml hexane through the top. Place the K-D apparatus on a hot water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the

vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml of hexane. Proceed with one of the following clean-up procedures.

10.2 Florisil Column Cleanup for Phthalate Esters

10.2.1 Place 100g of Florisil into a 500 ml beaker and heat for approximately 16 hours at 400°C. After heating transfer to a 500 ml reagent bottle. Tightly seal and cool to room temperature. When cool add 3 ml of distilled water which is free of phthalates and interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

10.2.2 Place 10g of this Florisil preparation into a 10 mm ID chromatography column and tap the column to settle the Florisil. Add 1 cm of anhydrous sodium sulfate to the top of the Florisil.

10.2.3 Preelute the column with 40 ml of hexane. Discard this eluate and just prior to exposure of the sodium sulfate layer to the air transfer the 2 ml sample extract onto the column, using an additional 2 ml of hexane complete the transfer.

10.2.4 Just prior to exposure of the sodium sulfate layer to the air add 40 ml hexane and continue the elution of the column. Discard this hexane eluate.

10.2.5 Next elute the phthalate esters with 100 ml of 20% ethyl ether/80% hexane (V/V) into a 500 ml K-D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml per minute for all fractions. Concentrate the collected fraction by standard K-D technique. No solvent exchange is necessary. After concentration and cooling, adjust the volume of the cleaned up extract to 10 ml in the concentrator tube and analyze by gas chromatography.

10.3 Alumina Column Cleanup for Phthalate Esters

10.3.1 Place 100 g of alumina into a 500 ml beaker and heat for approximately 16 hours at 400°C. After heating transfer to a 500 ml reagent bottle. Tightly seal and cool to room temperature. When cool add 3 ml of distilled water which is free from phthalates and

interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

10.2.2 Place 10g of this alumina preparation into a 10 mm ID chromatography column and tap the column to settle the alumina. Add 1 cm of anhydrous sodium sulfate to the top of the alumina.

10.2.3 Preelute the column with 40 ml of hexane. Discard this eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 ml sample extract onto the column, using an additional 2 ml of hexane to complete the transfer.

10.2.4 Just prior to exposure of the sodium sulfate layer to the air add 25 ml hexane and continue to elution of the column. Discard this hexane eluate.

10.2.5 Next elute the column with 140 ml of 20% ethyl ether/80% hexane (V/V) into a 500 ml K-D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml per minute for all fractions. Concentrate the collected fraction by standard K-D technique. No solvent exchange is necessary. After concentration and cooling adjust the volume of the cleaned up extract to 10 ml in the concentrator tube and

analyze by gas chromatography.

11. Gas Chromatography

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2-5 ul of the sample extract using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. Calculations

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, ug/l} = \frac{(A)\ (V_t)\ (D)}{(V_i)\ (V_s)}$$

where A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = volume of extract injected (ul)

V_t = Volume of total extract (ul)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting a interlaboratory method study to determine the accuracy and precision of this test procedure.

BIBLIOGRAPHY

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 1-Phthalates." Report for EPA Contract 68-03-2606 (In preparation).

TABLE I

GAS CHROMATOGRAPHY OF PHTHALATE ESTERS

Compound	Retention Time (min.) Column 1	Column 2	Detection Limit (ug/l) EC	FID
Dimethyl phthalate	2.03	0.95	0.11	19
Diethyl phthalate	2.82	1.27	0.13	31
Di-n-butyl phthalate	8.65	3.50	0.02	14
Benzyl butyl phthalate	6.94*	5.11**	0.02	15
Bis(2-ethylhexyl) phthalate	8.92*	10.5**	0.04	20
Di-n-octyl phthalate	16.2*	18.0**	0.11	31

Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long x 4 mm ID glass column with carrier gas at 60 ml/min flow rate. Column temperature is 180°C except where * indicates 220°C. Under these conditions R.T. of Aldrin is 5.49 min. at 180°C and 1.84 min at 220°C.

Column 2 conditions: Supelcoport 100/120 mesh coated with 3% OV-1 in a 180 cm long x 4 mm ID glass column with carrier gas at 60 ml/min flow rate. Column temperature is 200°C except where ** indicates 220°C. Under these conditions R.T. of Aldrin is 3.18 min. at 200°C and 1.46 min. at 220°C.

Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

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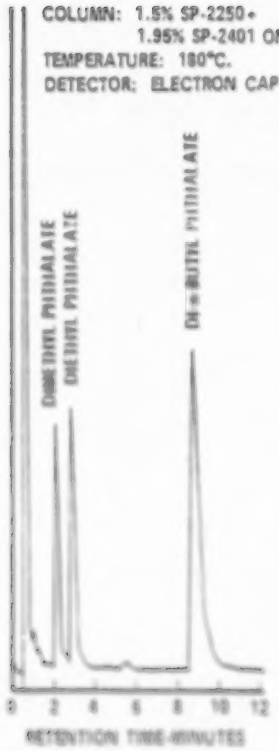

Figure 1. Gas chromatogram of phthalates

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COLUMN: 1.5% SP-2250 +
1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 180°C.
DETECTOR: ELECTRON CAPTURE

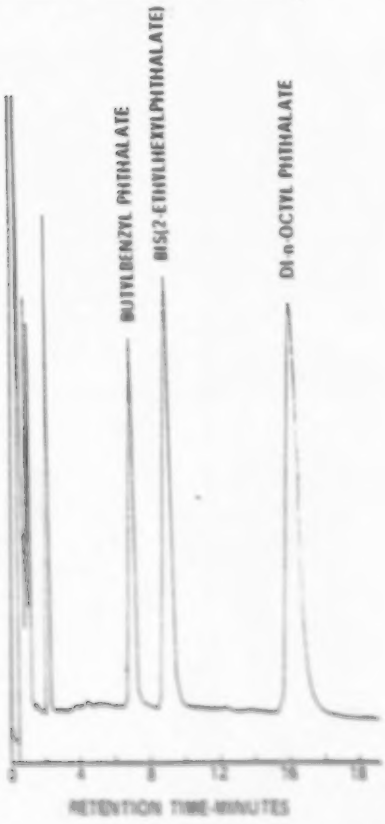

Figure 2. Gas chromatogram of phthalates